Superconductivity in the ternary intermetallics $YbPd_2Ge_2$, $LaPd_2Ge_2$, and $LaPt_2Ge_2$

G. W. Hull, J. H. Wernick, T. H. Geballe,* J. V. Waszczak, and J. E. Bernardini
Bell Laboratories, Murray Hill, New Jersey 07974
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Superconductivity is found to exist in the ternary intermetallics $YdPd_2Ge_2$, $LaPd_2Ge_2$, and $LaPt_2Ge_2$. Superconductivity-onset temperatures are 1.17, 1.12, and 0.55 K, respectively. Superconductivity was found neither in $YbCu_2Ge_2$ nor in bulk $CeCu_2Si_2$, the latter in contrast to previously published work.

I. INTRODUCTION

$CeCu_2Si_2$ appears to be a mixed-valent compound with the $ThCr_2Si_2$ structure in which transport and heat-capacity measurements show that the charge carriers have exceptionally large effective masses, two orders of magnitude greater than typically found in *d*-band metals. It has recently been reported to become superconducting,[1] a surprising result for such strongly interactive quasiparticles, and this is suggestive that the pairing interaction might be due to a nonconventional mechanism. We have been unable to reproduce the observed superconductivity in $CeCu_2Si_2$ above 0.47 K, the limit of our cryostat, and in conjunction with Dynes, have found the indication of only a trace of superconductivity down to 0.06 K, most likely due to the presence of a small fraction of an unidentified minority phase. In the course of this investigation we have discovered superconductivity in related RPd_2Ge_2-ordered intermetallic compounds where R is a rare earth, and in $LaPt_2Ge_2$, which possesses the tetragonal $ThCr_2Si_2$ structure ($BaAl_4$ type),[2,3] or a variant of this structure.[3] In the $ThCr_2Si_2$ structure, the Th atoms (or R atoms) occupy one set of equivalent sites. There are many ternary phases of the form RA_2X_2, where A = Pd, Pt, Rh, Ag, Cr, Mn, Fe, Co, Ni, and Cu and X = Si and Ge.[2,3] Of interest to us in this investigation was the occurrence of superconductivity in those phases not containing magnetic $3d$ elements. In particular, the lattice constant data[2] for $YbPd_2Ge_2$ suggested that Yb is, or nearly is, divalent (a $4f^{14}$ ion) but charge fluctuation or mixed-valent effects ($+2 \rightleftarrows +3$) perhaps could play an important role in the low-temperature properties.

II. EXPERIMENTAL AND RESULTS

The intermetallic compounds were prepared by induction-melting stoichiometric quantities of the constituents in vitreous carbon crucibles under one atmosphere of Ar. Melting losses were less than 1%. The as-prepared compound of $YbPd_2Ge_2$ was always multiphase and it was necessary to perform annealing experiments. Annealing was carried out for all of the compounds in sealed quartz ampoules. For $YbPd_2Ge_2$, a chip of Yb metal was also placed in the ampoule, but isolated from the compound, to prevent decomposition and to scavenge residual oxygen. Powder x-ray diffractometry (Cr $K\alpha$ radiation) was performed to confirm the structure and to ascertain the cleanliness of the samples and metallographic studies were also performed. Superconducting critical temperatures were determined by ac induction measurements and magnetic susceptibility measurements were made using the Faraday method.

III. $YbPd_2Ge_2$

The superconducting onset temperatures T_c and transition widths, ΔT_c, as well as other pertinent information are shown in Table I. The best material was obtained by annealing for two weeks at 670 °C (sample No. 11). Even so, the diffractometer traces exhibited several very weak lines that could be indexed on the basis of the presence of very small amounts of Yb, Pd_4Yb_3, PdGe, Pd_2Ge, and GeO_2. This was confirmed by metallographic studies which indicated the presence of small amounts of other phases. One extra line, at $d = 2.470$ Å, could not be indexed on the basis of any known phase of Yb, Pd, and Ge. The intensity of this line decreased rather dramatically with annealing, but could not be completely eliminated. In sample No. 11, this line was very, very weak. DTA measurements showed that $YbPd_2Ge_2$ undergoes three solid-state transitions before melting (at 732, 878, and 990 °C; evidence of melting obtained at 1425 °C, the limit of the DTA apparatus). We believe that the 2.470-Å line may be related to the presence of a small amount of one of the untransformed elevated temperature phases.

Magnetic susceptibility studies of as-prepared and annealed samples all showed Curie-Weiss contributions to the susceptibility, but the magnitude of this

TABLE I. Superconductivity results for $YbPd_2Ge_2$.

Sample No.	T_c (K)	ΔT_c	Fraction of sample superconducting (compared to Nb powder)	Remarks
1	1.33	0.31	0.5	As prepared
2	1.30	0.22	0.7	Annealed 24 h at 600 °C; no Yb atmosphere
3	1.23	0.18	0.8	Annealed 1 week at 600 °C; no Yb atmosphere
4	1.30	0.28	0.7	Annealed at 1000 °C for 24 h; no Yb atmosphere
5	1.18	0.17	1	Annealed 650 °C/114 h; no Yb atmosphere
6	1.27	0.30	0.7	As prepared
7	1.17	0.13	0.9	Annealed at 650 °C for 114 h; no Yb atmosphere
8	1.18	0.14	0.9	Annealed at 650 °C for 114 h; Yb atmosphere
9	1.27	0.31	0.6	No anneal
10	1.14	0.12	1	650 °C for 114 h; Yb atmosphere
11	1.17	0.19	1	670 °C for 2 weeks; Yb atmosphere

contribution decreased after annealing. It was the smallest for sample 11. If one assumes that the measured paramagnetic moments arise from Yb^{3+} (reasonable since $LaPd_2Ge_2$ shows no paramagnetic moments, see below) and that the moment of Yb^{3+} is equal to the free ion value of $4.5\mu_B/Yb$, the fraction of Yb^{3+} in each sample can be determined. In the as-prepared samples, 50% of the Yb is Yb^{3+}, consistent with the large amount of second phase seen in x-ray and metallographic studies of the sample. The lowest Yb^{3+} concentration ($\sim$16%) is obtained in the sample annealed for the longest time (No. 11). The susceptibility of the majority phase in this sample may be estimated by the following procedure. The measured susceptibility is fit to the form $\chi = C/(T+\Theta) + \chi_0$ by a least-squares method from 300 to 4.2 K; we assume that the Curie-Weiss term $C/(T+\Theta)$ is due to the small amount of second phase and that χ_0 is the temperature-independent susceptibility of the majority phase. A good fit to such an expression is obtained (standard deviation ±0.3%) making the above assumptions plausible. By this procedure we estimate that the susceptibility of the majority phase is weakly paramagnetic, $\chi_0 = 0.25 \times 10^{-6}$ emu/g.

IV. $LaPd_2Ge_2$ AND $LaPt_2Ge_2$

Superconductivity results for these two phases are shown in Table II. No extra diffraction lines were present in the annealed sample of $LaPd_2Ge_2$, although the metallographic studies revealed the presence of a needlelike precipitate. Basically, the sample was single phase. The as-prepared sample differed little from the annealed and it was essentially

TABLE II. Superconductivity results for $LaPd_2Ge_2$ and $LaPt_2Ge_2$.

	T_c (K)	ΔT_c	Remarks
$LaPd_2Ge_2$	1.12	0.04	Annealed at 670 °C for 5 days
$LaPt_2Ge_2$	0.55	· · ·	Annealed at 650 °C for 5 days

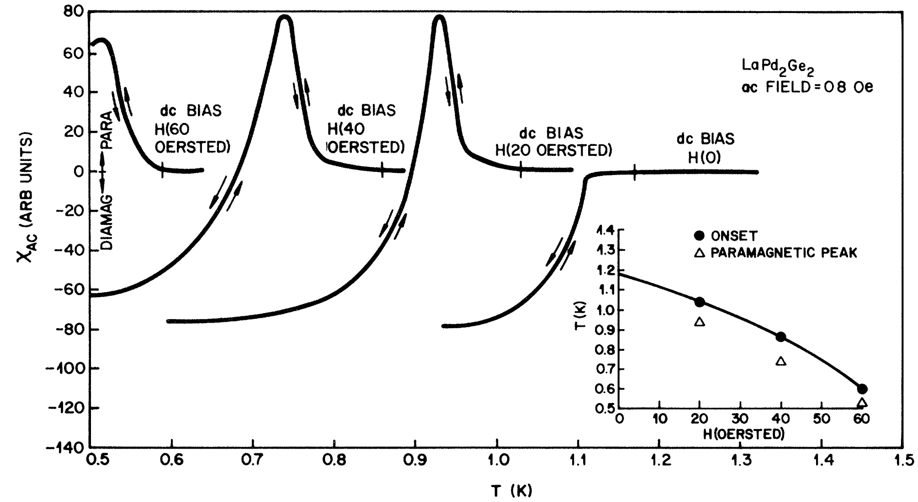

FIG. 1. Low-frequency ac susceptibility of $LaPd_2Ge_2$ as a function of temperature without and with a dc bias field. Note the development of a reversible differential paramagnetic signal.

single phase. The diffractometer trace of the annealed sample of $LaPt_2Ge_2$ showed several weak extra lines that could be indexed on the basis of La_2O_3, Ge, and $LaGe_2$. The structure of $LaPt_2Ge_2$ is tetragonal, but a variant of the $ThCr_2Si_2$ structure.[4]

The magnetic susceptibility of $LaPd_2Ge_2$ exhibited a small Curie contribution that is attributed to a low level of paramagnetic impurities (perhaps 20–50 ppm Fe). Otherwise the intrinsic susceptibility is temperature independent and 0.1×10^{-6} emu/g.

$LaPt_2Ge_2$ exhibits a weakly temperature dependent diamagnetic susceptibility below 300 K. A small Curie-Weiss contribution was observed below 50 K probably caused by a small amount of Fe impurity (20 ppm). The absolute value χ_g for this sample at room temperature is -0.02×10^{-6} emu/g $\pm 20\%$.

The susceptibilities of $LaPt_2Ge_2$ and of $LaPd_2Ge_2$ are typical of low density states metals and are slightly smaller than the estimated susceptibility of $YbPd_2Ge_2$.

The superconducting transitions as measured by a low-frequency (25 Hz) ac bridge for powdered samples of $LaPd_2Ge$ in low applied fields showed a surprising reversibility as demonstrated by the differential paramagnetic signals shown in Fig. 1. This high degree of reversibility for the entry and exit of small amounts of flux is rarely found in intermetallic compounds. The very low critical field curve shown in the inset suggests that the material may in fact be a type 1 superconductor.

V. $CeCu_2Si_2$

Steglich *et al.*[1] recently reported superconductivity in $CeCu_2Si_2$ ($T_c = 0.5$ K). This material exhibits low-temperature transport properties suggestive of Ce "unstable 4*f* shell" behavior. The samples Steglich *et al.* studied were prepared by arc melting and their results were obtained on both unannealed and annealed samples. We have not been able to reproduce their superconductivity results. More specifically, a sample of $CeCu_2Si_2$ annealed at 900 °C for five days (similar to the Steglich *et al.* annealed sample) was normal down to 0.47 K. The sample reported by Steglich *et al.* became superconducting above 0.5 K. Further measurements in a dilution refrigerator down to 0.060 K by Dynes showed no evidence for bulk superconductivity although a noticeable decrease in resistance occurred. This decrease could be due to a smeared out superconducting transition of a minority second phase.

The diffractometer trace for our sample exhibited very weak extra diffraction peaks that could be indexed on the basis of the presence of Cu_3Si, $CeCu_2$, $CeCu_6$, and CuO as extra phases. The magnetic susceptibility exhibited a temperature-dependent paramagnetic contribution that did not fit Curie-Weiss behavior over any significant temperature range. This may be due to the fact that the crystal-field splittings of Ce^{3+} are frequently on the order of 100 K. On the other hand, $CeCu_2$ and $CeCu_6$, as impurity phases may be contributing to the above susceptibility behavior. $CeCu_2$ has been shown to exhibit a non-Curie-Weiss temperature-dependent susceptibility[5] and it is likely that $CeCu_6$ would exhibit similar behavior.

VI. $YbCu_2Ge_2$

A sample of $YbCu_2Ge_2$, annealed at 670 °C for five days, did not exhibit superconductivity down to 0.47 K.

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[*]Also at Department of Applied Physics, Stanford University, Stanford, Cal. 94305.

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