Superconductivity in the ternary rare-earth (Y, La, and Lu) compounds $R\mathrm{Pd_2Si_2}$ and $R\mathrm{Rh_2Si_2}$

T. T. M. Palstra, G. Lu,* A. A. Menovsky, G. J. Nieuwenhuys, P. H. Kes, and J. A. Mydosh
Kamerlingh Onnes Laboratorium der Rijks-Universiteit Leiden, 2300 RA Leiden, The Netherlands
(Received 18 November 1985)

We have investigated the superconducting and metallurgical properties of the ternary compounds $R\mathrm{Pd_2Si_2}$ and $R\mathrm{Rh_2Si_2}$ with R=Y, La, and Lu. All $R\mathrm{Pd_2Si_2}$ compounds and $\mathrm{LaRh_2Si_2}$ were found to be type-I superconductors below 1 K. A detailed metallurgical analysis shows that segregation of second phases can easily mask the intrinsic (stoichiometric ratio 1:2:2) intermetallic-compound properties. Two sample-preparation techniques, viz., single crystals and off-stoichiometry, were utilized to establish where bulk superconductivity occurs. The type-I behavior of these compounds is explained with an analogous model as is used for the heavy-fermion superconductors $\mathrm{CeCu_2Si_2}$ and $\mathrm{URu_2Si_2}$.

I. INTRODUCTION

The ternary (1:2:2) compounds RT_2X_2, with R a lanthanide or actinide element, T a transition metal, and X=Si, Ge, or Sn, have recently attracted much attention because of their interesting superconducting and magnetic properties.[1] In this paper we focus on the superconducting properties and the related metallurgical problems of the nonmagnetic compounds with R=Y, La, or Lu and T=Rh or Pd and X=Si. We have found that all $R\mathrm{Pd_2Si_2}$ compounds are type-I superconductors with T_c below 1 K, an observation not reported in literature thus far.

The superconductivity of the $R\mathrm{Rh_2Si_2}$ compounds has been a controversial issue. Two investigations of $\mathrm{LaRh_2Si_2}$ have reported T_c's at about 4 K.[2,3] However, a more detailed investigation ascribed this superconductivity to second phases.[4] From our experiments we have determined that single-phase $\mathrm{LaRh_2Si_2}$ is a type-I superconductor, but with a much lower T_c, namely, 74 mK. Furthermore, we will show that the stability regime of the $\mathrm{LaRh_2Si_2}$ stoichiometry is very small, leading to an easy formation of second phases. Two of the second phases are superconductors, one at 4.0 K and the other at 0.36 K, and thus inclusion of these phases can explain the conflicting behavior.[2–4]

II. EXPERIMENTAL PROCEDURES

The polycrystalline samples were prepared by arc melting the constituent elements in a Ti-gettered argon atmosphere. All polycrystalline samples were vacuum-annealed for about seven days at 900 °C. In addition to the stoichiometric samples, nonstoichiometric $\mathrm{LaRh_2Si_2}$ were also prepared of formula $\mathrm{La_{1+x}Rh_2Si_2}$ with $x=-0.05$, -0.02, 0.01, and 0.02 and $\mathrm{LaRh_{2-x}Si_{2+x}}$ with $x=-0.02$ and 0.02. Finally, three single crystals of $\mathrm{LaRh_2Si_2}$, $\mathrm{LaPd_2Si_2}$, and $\mathrm{LuPd_2Si_2}$ were grown with a "tri-arc" adopted Czochralski method.[5] The samples were characterized by x-ray powder diffraction, optical microscope, and microprobe analysis.

The superconducting properties were measured in a ^{3}He cryostat via (i) ac susceptibility with a driving field of about 0.5 Oe, (ii) magnetization by integrating the voltage induced in the pick-up coils when ramping a dc magnetic field, and (iii) resistivity with a four-point probe method. The temperature was determined with a calibrated carbon-glass thermometer and a dc magnetic field could be applied up to 1 T. Some $\mathrm{LaRh_2Si_2}$ samples were additionally studied in a dilution refrigerator down to 20 mK with ac susceptibility. The normal-state magnetic properties were investigated with a Foner vibrating-sample magnetometer from 1.5 K to room temperature in magnetic fields up to 5 T.

III. EXPERIMENTAL RESULTS

The $R\mathrm{Rh_2Si_2}$ and $R\mathrm{Pd_2Si_2}$ compounds are formed in a strong exothermic reaction. The x-ray powder diffractograms can be indexed based upon the tetragonal $\mathrm{ThCr_2Si_2}$-type structure, and the resulting lattice parameters are given in Table I. There are no indications for a random-site occupation of the Si and Rh or Pd atoms. Additionally, a low-temperature or high-temperature modification is not expected because samples both annealed and quenched from the melt have only reflections with an even sum of Miller indices. This condition follows from the body-centered symmetry of the $\mathrm{ThCr_2Si_2}$-type structure and is neither fulfilled for the primitive tetragonal $\mathrm{CaBe_2Ge_2}$-type structure nor for a random-site occupation of the Si and Rh or Pd atoms.

All polycrystalline samples contain small segregations of second phases with an estimated volume fraction less than 1%, invisible in x-ray powder diffractograms, but clearly detectable with an optical microscope or microprobe analysis. These second phases are either R oxides or compounds with a different composition than the matrix. They are segregated either along the grain boundaries or along parallel planes (probably the a-b basal plane) within microcrystallites. The result of the heat treatment of 900 °C, most thoroughly studied for $\mathrm{LaRh_2Si_2}$, is a growth of the microcrystallites to much larger crystals and a displacement of the segregations within the crystallites to the grain boundaries.

The three single crystals $\mathrm{LaRh_2Si_2}$, $\mathrm{LaPd_2Si_2}$, and

TABLE I. Lattice parameters and unit-cell volume of the ternary (1:2:2) compounds $R\mathrm{Pd_2Si_2}$ and $R\mathrm{Rh_2Si_2}$, with R=Y, La, or Lu. Also indicated are the superconducting transition temperatures T_c and the critical fields $H_c(0)$.

	a (Å)	c (Å)	V (Å^3)	T_c (K)	$\mu_0 H_c(0)$ (mT)
$\mathrm{YPd_2Si_2}$	4.129	9.84	167.8	0.47	5.4
$\mathrm{LaPd_2Si_2}$	4.283	9.88	181.2	0.39	3.1
$\mathrm{LuPd_2Si_2}$	4.089	9.85	164.7	0.67	7.0
$\mathrm{YRh_2Si_2}$	4.031	9.92	161.2	<0.33	
$\mathrm{LaRh_2Si_2}$	4.112	10.29	174.0	0.074	0.73
$\mathrm{LuRh_2Si_2}$	4.090	10.18	170.3	<0.33	

$\mathrm{LuPd_2Si_2}$ were checked with Laue photographs and microprobe analysis. These crystals contained *no* second phases except for a thin surface layer of an R oxide. This surface layer can easily be removed by etching or polishing. Therefore, no additional heat treatment is necessary and these samples may serve as reference materials with respect to the polycrystals, concerning their superconducting properties.

For one compound, $\mathrm{LaRh_2Si_2}$, we systematically studied the results of off-stoichiometry. Microprobe analysis showed that deviations of 1% or more from the stoichiometric ratio (1:2:2) always resulted in segregations of a compound with a composition in agreement with the deviations from stoichiometry. The second phases are again segregated on the grain boundaries or on parallel planes within the microcrystallite, and thus can easily form a continuous three-dimensional network.

The three $R\mathrm{Pd_2Si_2}$ compounds become superconducting at transition temperatures of $T_c=0.67$ K for $\mathrm{LuPd_2Si_2}$, $T_c=0.39$ K for $\mathrm{LaPd_2Si_2}$, and $T_c=0.47$ K for $\mathrm{YPd_2Si_2}$ (see Fig. 1). To check whether the superconductivity is a bulk property, we prepared single-crystal samples, which are completely single phase. These crystals have identical critical temperatures as the polycrystalline samples. The dc-field dependence of the ac susceptibility below T_c is shown in Fig. 2 and exhibits a pronounced positive peak in each field direction. This peak can be understood in terms of the fully reversible hysteresis loops on the magnetization curve, also shown in Fig. 2. Such a magnetization curve demonstrates that these compounds are type-I superconductors. A parabolic fit to the temperature dependence of the critical field $H_c(T)$ versus T yields $\mu_0 H_c(0)=7.0$ mT for $\mathrm{LuPd_2Si_2}$, $\mu_0 H_c(0)=3.1$ mT for $\mathrm{LaPd_2Si_2}$, and $\mu_0 H_c(0)=5.4$ mT for $\mathrm{YPd_2Si_2}$, as illustrated in Fig. 3. For $\mathrm{YRh_2Si_2}$ and $\mathrm{LuRh_2Si_2}$ no superconductivity was observed down to 0.33 K.

For $\mathrm{LaRh_2Si_2}$ the situation is more complicated. We prepared three stoichiometric, polycrystalline samples. Sample 1 was measured with ac susceptibility down to 20 mK and the other two down to 330 mK. Sample 1 contained the least segregations of these three samples as observed by microprobe analysis and became superconducting at 74 mK (see Fig. 1). The field dependence of the ac susceptibility exhibits positive peaks, similar to those of $R\mathrm{Pd_2Si_2}$, indicating a type-I behavior. Sample 2 was measured before annealing and became superconducting at 360 mK. After annealing we found only a weak onset of superconductivity at this temperature. Sample 3, which was annealed, did not become superconducting down to 330 mK.

In order to resolve the intrinsic superconducting prop-

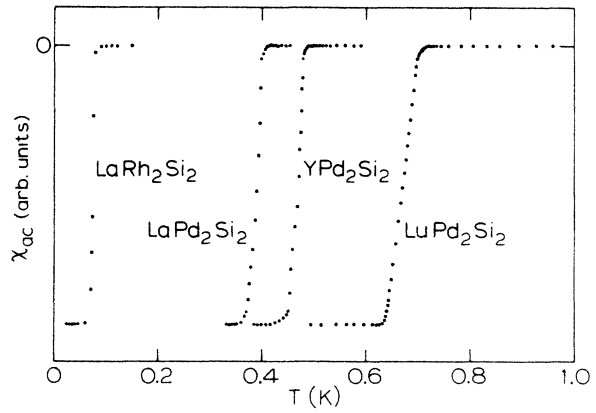

FIG. 1. Superconducting transitions of $R\mathrm{Pd_2Si_2}$, with R=Y, La, or Lu and $\mathrm{LaRh_2Si_2}$ determined from ac susceptibility versus temperature curves.

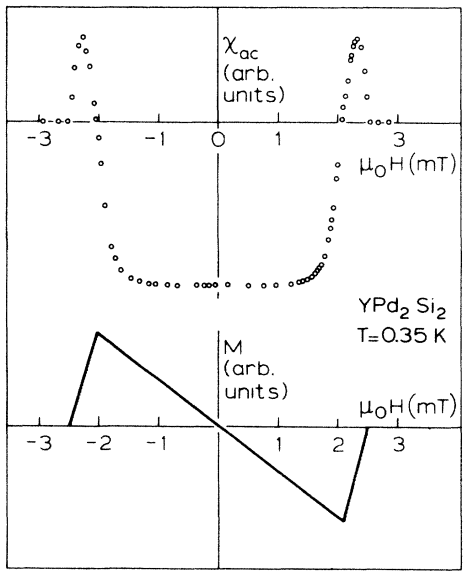

FIG. 2. Magnetic field dependence of the ac susceptibility and the magnetization of $\mathrm{YPd_2Si_2}$ at 350 mK.

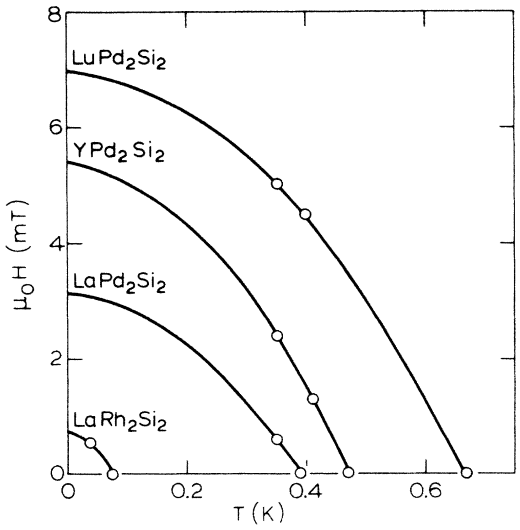

FIG. 3. Critical fields for RPd$_2$Si$_2$, with R=Y, La, or Lu and LaRh$_2$Si$_2$. The solid lines represent a parabolic fit: $H_c(T)/H_c(0)=1-(T/T_c)^2$.

erties of LaRh$_2$Si$_2$, we also prepared nonstoichiometric samples of formula La$_{1+x}$Rh$_2$Si$_2$ and LaRh$_{2-x}$Si$_{2+x}$. These samples lie along the two thick lines through LaRh$_2$Si$_2$ in the ternary phase diagram given in Fig. 4. We observed that the La$_{1+x}$Rh$_2$Si$_2$ samples with excess La become superconducting at 0.36 K, while the samples with La deficit did not become superconducting down to 0.33 K. For the compounds LaRh$_{2+x}$Si$_{2-x}$ we found a superconducting transition at 4.0 K for the Si-rich samples, but no superconductivity for the Rh-rich samples. Finally we measured the ac susceptibility of the LaRh$_2$Si$_2$ single crystal which should reveal the intrinsic superconducting behavior because of the total absence of any second phase. The single crystal became superconducting at 74 mK.

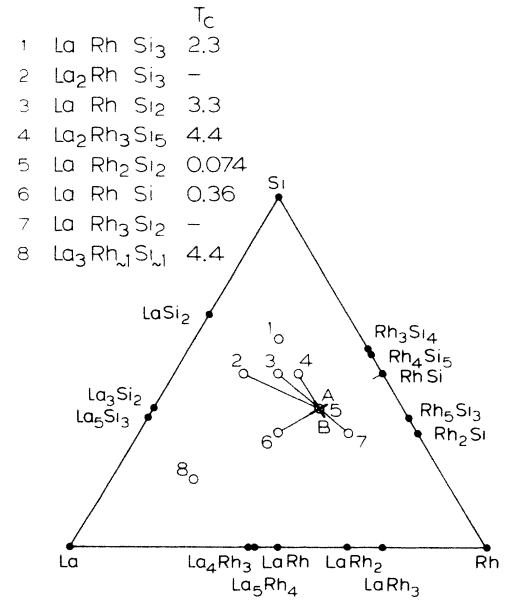

FIG. 4. Ternary phase diagram of the system La-Rh-Si according to Ref. 4. The thin solid lines represent the tie lines of LaRh$_2$Si$_2$ to neighboring compounds. The lines A and B represent compounds of formula La$_{1+x}$Rh$_2$Si$_2$ and LaRh$_{2-x}$Si$_{2+x}$, respectively. The superconducting transition temperatures of the eight identified ternary phases are indicated.

Additionally, we have performed very accurate magnetization measurements on all the variously prepared samples of LaRh$_2$Si$_2$. There were no indications for any magnetic phase transitions as were reported earlier.[3] The magnetization had little temperature dependence and a value of 1.5×10^{-4} emu/mol, indicating a weak Pauli paramagnetism.

IV. DISCUSSION

A. Metallurgy

The La-Rh-Si system is one of the few ternary compounds for which an isothermal-section phase diagram has been established.[4] Here, eight ternary compounds were identified, five of which were found to be superconductors (see Fig. 4). In contrast to these results, the compounds LaRhSi and LaRh$_2$Si$_2$ have also been claimed to be superconductors with T_c=4.35 and 3.9 K.[2,3] We have concentrated our efforts on the compound LaRh$_2$Si$_2$ not only to resolve the question of superconductivity, but also to investigate the causes of the metallurgical difficulties which have led to these contradictory results.

The basic problem of the metallurgy of LaRh$_2$Si$_2$ is the extremely small range of stoichiometry. This property leads to the formation of second phases, already for off-stoichiometric preparation of the samples of order of 1%. These second phases not only arise from systematic errors caused by weighing errors, oxides in the starting materials and melting losses, but also from small concentration fluctuations in the melt. Accordingly, we found both La-rich and La-poor precipitates in an as-quenched stoichiometric LaRh$_2$Si$_2$ sample. Consequently, an annealing procedure is necessary, although we believe that a heat treatment at 900 °C is too low in view of the estimated melting temperature of 1600 °C. During the heat treatment the segregations are directed to the grain boundaries where the concentration fluctuations can be smeared out. Nevertheless, this may cause a percolated network through the sample.

Such a percolated network can short-circuit the resistance of the sample and may shield magnetic fields. Thus, resistivity and ac-susceptibility measurements must be interpreted with precaution. Two other frequently used techniques, namely specific heat and Meissner-effect measurements, are more difficult below 1 K, and could lead to complications in case of large transition width ΔT_c or strong flux-pinning effects.

We have approached the question of bulk superconductivity in LaRh$_2$Si$_2$ via two other methods. First, we used off-stoichiometric samples to contrast the intrinsic properties. Here, the results for T_c from the ac susceptibility need to be closely related to the detailed analysis of the sample quality and segregations. This method has the additional advantage that it also provides information about

the neighboring phases. Second, we have studied "ideal" samples by preparing single crystals with a specially adopted "tri-arc" Czochralski method. These single crystals grow under the near-equilibrium conditions that are highly suitable for producing single-phase specimens because the range of stoichiometry is small. This method has the further advantage of the purifying effect of the Czochralski method.

With our detailed knowledge of the ternary La-Rh-Si phase diagram, we conclude from the observed behavior of the polycrystals and single crystals that (i) stoichiometric $LaRh_2Si_2$ is a type-I superconductor with $T_c=74$ mK, (ii) the superconductivity at 0.36 K must be attributed to segregations of LaRhSi, and (iii) the observed superconductivity[2,3] at 4.0 K can be ascribed to segregations of $La_2Rh_3Si_5$.

In our opinion, the different transition temperatures must be caused by different ternary phases and *not* by a range of transition temperatures over the range of stoichiometry.[6] The latter would require that T_c could vary by a factor 50 over the extremely small range of stoichiometry less than 1%. The former is further supported by the fact that both the single crystal and the purest polycrystal have the same T_c value of 74 mK.

The contradictory results reported on $LaRh_2Si_2$ can neither be explained with a high-temperature or low-temperature modification of the $ThCr_2Si_2$- and $CaBe_2Ge_2$-type crystal structures as found for $LaIr_2Si_2$,[7] nor with a mixed site occupancy of the Rh and Si sites. For in both cases, powder diffractograms should show Miller indices with an odd sum, which was not the case with our annealed samples nor with rapidly quenched samples.

In order to check the superconducting properties of LaRhSi, we have prepared a stoichiometric polycrystalline (1:1:1) sample. This sample became indeed superconducting at 0.36 K. Our result is in agreement with the observations of Braun,[4] who found no superconductivity down to 1.2 K. However, Chevalier *et al.*[2] report a superconducting transition temperature $T_c=4.35$ K. A detailed metallurgical analysis by Braun, and likewise by ourselves, attributes this result to the formation of second phases. We conclude that the intrinsic transition temperature of LaRhSi is 0.36 K.

B. Superconductivity

Consistent with our present results, type-I superconductivity (Ginzburg-Landau parameter $\kappa_{GL}<0.7$) had earlier been reported for $LaPd_2Ge_2$.[8] This behavior stands in total contrast to the type-II superconductivity of the isostructural heavy-fermion compounds $CeCu_2Si_2$ ($\kappa_{GL}\approx 22$) (Ref. 9) and URu_2Si_2 ($\kappa_{GL}\approx 33$).[10] The distinction between type-I and type-II behavior seems to be critically dependent on whether the superconductivity is carried by light electrons (Y, La, Lu) or by heavy electrons (Ce, U).

The intrinsic superconducting properties of these compounds are defined by the value of the Ginzburg-Landau parameter κ_{GL}. We explicitly exclude mean-free-path effects (see below), and thus $\kappa_{GL}=\kappa_0=0.96\lambda_L(0)/\xi_0$, with $\lambda_L(0)$ the London penetration depth and ξ_0 the coherence length (Ref. 11). $\lambda_L(0)$ can be calculated from the London equation $\lambda_L^2(0)=m^*/\mu_0 ne^2$ with m^* the effective electron mass, μ_0 the permeability constant, n the conduction-electron density, and e the electron charge. In Bardeen-Cooper-Schrieffer (BCS) theory the coherence length ξ_0 is given by $\xi_0=0.18\hbar v_F/k_B T_c$ with $\hbar$ Planck's constant, v_F the Fermi velocity, k_B Boltzmann's constant, and T_c the superconducting transition temperature. This leads to the universal relation:

$$\kappa_0=3.21\times 10^{22} T_c (m^*/m_e)^{3/2} n^{-1/2} k_F^{-1} .$$

Assuming a spherical Fermi surface $n=k_F^3/3\pi^2$ and setting $T_c=0.5$ K the above equation can be reduced to $\kappa_0=8.72\times 10^{22}(m^*/m_e)^{3/2}/k_F^{5/2}$. For the 1:2:2 compounds there are six conduction electrons per two formula units per unit cell ($4\times 4\times 10=160$ Å^3), yielding a Fermi vector $k_F=1.04$ Å^{-1}. Thus, we obtain a relation between the Ginzburg-Landau parameter κ_0 and the effective mass of the conduction electrons for these compounds, viz., $\kappa_0=7.9\times 10^{-3}(m^*/m_e)^{3/2}$. Comparatively, for $CeCu_2Si_2$ a value of $\kappa_0=10$ was reported,[12] resulting for our model in a mass enhancement of 118, which is in close agreement with other calculations.[12]

From the above analysis the distinction between type-I and type-II superconductivity takes place at a mass enhancement of about $m^*/m_e=20$. As this mass enhancement is unlikely for the compound presently investigated, type-I behavior may be expected as a general property for the nonmagnetic RT_2Si_2-type compounds. We stress that our analysis assumes a spherical Fermi surface, and thereby leads to only a rough estimate of the k_F. Nevertheless, a factor of 2 error in k_F would not invalidate our conclusion of the type-I behavior for these type of compounds.

Furthermore, our analysis neglects mean-free-path effects, which have been shown to be of minor importance in case of heavy-fermion superconductors. Such effects require[13] that an additional term must be included in the Ginzburg-Landau parameter as $\kappa_{GL}-\kappa_0=2.4\times 10^6\gamma^{1/2}\rho$. For type-I superconductors this term is also less than $\frac{1}{2}\sqrt{2}$, with γ in J/m^{3}K^2 and ρ in Ωm, or $\gamma^{1/2}\rho<3\times 10^{-7}$. The value of γ can be derived from the relation $\gamma=2.12\mu_0 H_c^2(0)T_c^{-2}$, which is nearly the same for all four superconducting compounds. Using the values for $LuPd_2Si_2$, namely, $T_c=0.67$ K and $\mu_0 H_c(0)=7\times 10^{-3}$ T, we obtain $\gamma=184$ J/m^{3}K^2 (=18.2 mJ/molK^2) which is larger than our experimentally observed value of $\gamma=78$ J/m^{3}K^2. This discrepancy may be related to strong coupling effects and to a nonspherical Fermi surface. Using the experimental value for γ, we derive that $\rho<3.4$ $\mu\Omega$cm. Our resistivity measurements on a single crystal of $LuPd_2Si_2$ show highly anisotropic residual values, namely $\rho(4\text{ K})=5.9$ $\mu\Omega$cm along the a axis and 12 $\mu\Omega$cm along the c axis. This result indicates a correspondingly anisotropic Fermi surface, and that the anisotropy of the mean-free-path effects has not been incorporated correctly. Consequently, there must be a crystal direction along which a lower residual resistivity is present. Alternatively, we must assign anisotropic values to γ, which is an averaged quantity over the Fermi surface. Critical-field measurements on single-crystal samples are warranted to resolve this latter possibility.

Finally, we note that the superconducting transition temperature T_c is strongly dependent on the actual electron-phonon interaction, and for the $R\mathrm{Pd_2Si_2}$ compounds there is a relation between T_c and the unit-cell volume V (see Table I). As the density of states is nearly the same for all four superconducting compounds $[N(E_F) \sim \gamma \sim H_c^2/T_c^2]$, we expect the superconductivity for $\mathrm{YRh_2Si_2}$ and $\mathrm{LuRh_2Si_2}$ might likewise be expected in the millikelvin range.

In conclusion, we have found bulk superconductivity for single-phase $R\mathrm{Pd_2Si_2}$ with $R=$Y, La, or Lu and for $\mathrm{LaRh_2Si_2}$. The observed type-I behavior may be regarded as a general property of this type of nonmagnetic R compounds and serves as a simple reference for the heavy-fermion compounds $\mathrm{CeCu_2Si_2}$ and $\mathrm{URu_2Si_2}$ with respect to their superconducting properties.[14]

ACKNOWLEDGMENTS

We wish to acknowledge the technical assistance of C. E. Snel, H. J. Tan, and T. J. Gortenmulder. This work is part of the research program of the Nederlandse Stichting voor Fundamenteel Onderzoek der Materie (FOM).

*Permanent address: Department of Physics, Peking University, Beijing, People's Republic of China.

[1]See, for example, H. Pinto, M. Melamud, M. Kuznietz, and H. Shaked, Phys. Rev. B **31**, 508 (1985), and references therein.

[2]B. Chevalier, P. Lejay, J. Etourneau, and P. Hagenmuller, Mater. Res. Bull. **18**, 315 (1983).

[3]I. Felner and I. Nowik, Solid State Commun. **47**, 831 (1983).

[4]H. F. Braun, J. Less-Common. Met. **100**, 105 (1984).

[5]A. A. Menovsky and J. J. M. Franse, J. Cryst. Growth **65**, 286 (1983).

[6]M. Ishikawa, H. F. Braun, and J. L. Jorda, Phys. Rev. B **27**, 3092 (1983).

[7]H. F. Braun, N. Engel, and E. Parthé, Phys. Rev. B **28**, 1389 (1983).

[8]G. W. Hull, J. H. Wernick, T. H. Geballe, J. V. Waszczak, and J. E. Bernardini, Phys. Rev. B **24**, 6715 (1981).

[9]F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Phys. Rev. Lett. **43**, 1892 (1979).

[10]T. T. M. Palstra, A. A. Menovsky, J. van den Berg, A. J. Dirkmaat, P. H. Kes, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Rev. Lett. **55**, 2727 (1985).

[11]M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).

[12]U. Rauchschwalbe, W. Lieke, C. D. Bredl, F. Steglich, J. Aarts, K. M. Martini, and A. C. Mota, Phys. Rev. Lett. **49**, 1448 (1982).

[13]W. B. Buckel, *Supraleitung* (Physik-Verlag, Weinheim, 1984), p. 145.

[14]A more detailed comparison is given in T. T. M. Palstra, Ph.D. thesis, University of Leiden, 1986 (unpublished).