Superconductivity and magnetism in the $La_{2-x}Nd_xRh_3Si_5$ system

N.G. Patil, K. Ghosh, and S. Ramakrishnan
Tata Institute of Fundamental Research, Bombay 400005, India
(Received 23 May 1995)

It is now well known that the compounds that belong to the $R_2Fe_3Si_5$ series exhibit unusual superconducting and magnetic properties. Although a reasonable number of studies have been made on this series, similar efforts on another series, namely, $R_2Rh_3Si_5$, whose structure is closely related to $R_2Fe_3Si_5$, have not been made. In this paper, we have established the bulk superconductivity in $La_2Rh_3Si_5$ below 4.4 K and bulk antiferromagnetism in $Nd_2Rh_3Si_5$ below 2.7 K, from resistivity, susceptibility, and heat-capacity studies. The superconducting transition temperature of (T_c) $La_2Rh_3Si_5$ decreases with the Nd substitution for La and we have analyzed this T_c dependence using Abrikosov and Gor'kov theory with crystal-field contributions. The estimated value of the interaction between the conduction electrons and the rare-earth spin (J_{sf}) is 37 meV, which is adequate to suppress the coexistence of superconductivity and antiferromagnetism in $La_{2-x}Nd_xRh_3Si_5$ alloys above 0.6 K. Finally, we have also analyzed the temperature dependence of the upper critical field of Nd-doped $La_2Rh_3Si_5$ alloys using a theory which incorporates spin-orbit coupling with an additional pair breaking parameter.

I. INTRODUCTION

Large number of studies have been made to understand the remarkable properties of ternary silicides, which form in a variety of crystal structures.[1,2] Some of these compounds undergo superconducting transition at low temperatures.[3,4] Considerable efforts have been made to understand the superconductivity and magnetism exhibited by compounds belonging to the $R_2Fe_3Si_5$ system.[5–8] In this family the Fe atoms do not carry any moment but help in building a large density of states at the Fermi level.[9] It is now well established that a member of this series, namely, $Tm_2Fe_3Si_5$ (Ref. 10) is the first reentrant antiferromagnetic superconductor. A recent study claims that an antiferromagnet $Er_2Fe_3Si_5$ (Ref. 11) (below 2.5 K) becomes superconducting below 1 K. Although many investigations were made in the $R_2Fe_3Si_5$ series, only very few attempts have been made to understand the superconductivity in other silicides.[12–14] In particular, we are aware of only two reports on the superconductivity and magnetism of the $R_2Rh_3Si_5$ (Refs. 12 and 14) series, whose structure is closely related to the $R_2Fe_3Si_5$ family. Although, both iron silicides and rhodium silicides are derived from a $BaAl_4$-type structure, the former exist in the tetragonal structure (space group $P4/mnc$), while the latter exist in the orthorhombic structure (space group $Ibam$). Since the compounds belonging to the $R_2Fe_3Si_5$ series exhibit unusual superconducting and magnetic properties, it will be of interest to study the magnetism and superconductivity in the $R_2Rh_3Si_5$ family. With this in view, as a part of our detailed study on this series, we report our resistivity, susceptibility, and heat-capacity measurements on $La_2Rh_3Si_5$, $Nd_2Rh_3Si_5$, and alloys formed by mixing these two compounds.

II. EXPERIMENTAL DETAILS

Samples of $La_{2-x}Nd_xRh_3Si_5$ (x=0–2) were made by melting the individual constituents (taken in stoichiometric proportions) in an arc furnace under a high-purity argon atmosphere. The purity of the La, Nd, and Rh was 99.9%, whereas the purity of Si was 99.999%. The alloy buttons were remelted five to six times to ensure proper mixing. The samples were annealed at 900° C for a week. The x-ray powder-diffraction pattern of the samples did not show the presence of any parasitic impurity phases, and the lattice constants a, b, and c decreased linearly with the substitution of Nd for La. The dependence of the lattice constants a, b, and c, on the concentration x in $La_{2-x}Nd_xRh_3Si_5$ is shown in Fig. 1. Their values for x=0 and 2 agree with those published from a previous study.[11] The temperature dependence of susceptibility (χ) was measured using the Faraday method in a field of 4 kOe in the temperature range from 3.5 to 300 K. The ac susceptibility was measured using a home built susceptometer[15] from 1.5 to 20 K. The resistivity was measured using a four-probe dc technique with contacts made using silver paint on a cylindrical sample of 2-mm diameter and 10-mm length. The temperature was measured using a calibrated Si diode (Lake Shore Inc., USA) sensor. The sample voltage was measured with a nanovoltmeter (model 182, Keithley, USA) with a current of 25 mA using a 20-ppm stable (Hewlett Packard, USA) current source. All the data were collected using an IBM-compatible PC/AT via IEEE-488 interface. The heat-capacity in zero field between 1.7 and 40 K was measured using an automated adiabatic heat pulse method. A calibrated germanium resistance thermometer (Lake Shore Inc., USA) was used as the temperature sensor in this range.

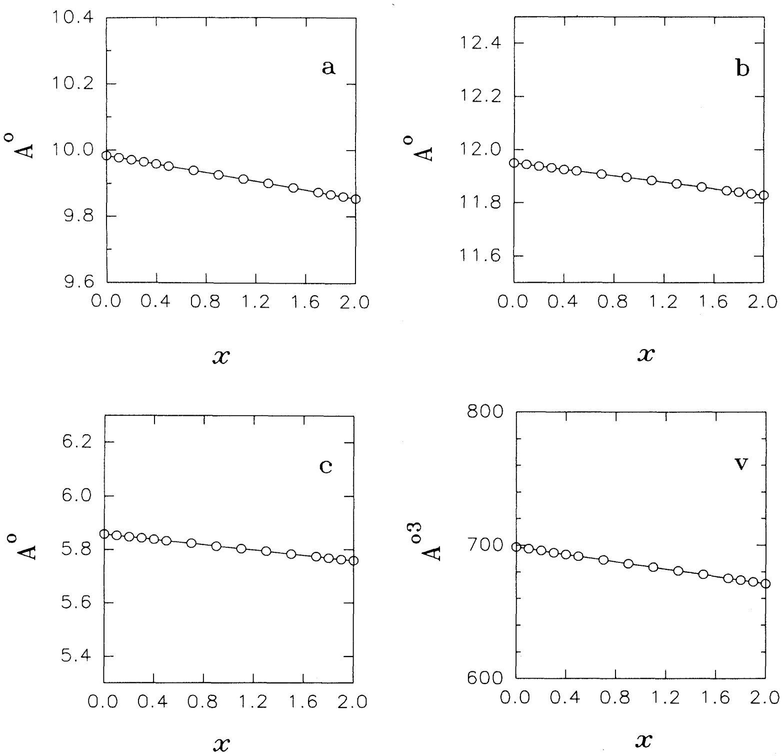

FIG. 1. Variation of lattice constants a, b, c, and volume V with Nd concentration (x) in the $La_{2-x}Nd_xRh_3Si_5$ system.

III. RESULTS AND DISCUSSION

A. Normal and superconducting state properties of $La_2Rh_3Si_5$

1. Magnetic susceptibility studies

The temperature dependence of the dc magnetic susceptibility (χ_{dc}) of $La_2Rh_3Si_5$ sample in a field of 4 kOe from 3.5 to 300 K is shown in Fig. 2. The inset shows ac susceptibility behavior of the same sample at low temperature in an ac field of 2 Oe. This inset clearly shows the diamagnetic transition below 4.4 K, which is in agreement with the previously reported value.[14] The normal state χ_{dc} of this sample has a temperature-independent value of 1.7×10^{-4} emu/mol down to 10 K. Below 10 K, there is a small increase (3%) in χ_{dc}, which we attribute to the presence of paramagnetic impurities in this sample. The temperature-independent χ_{dc} has contributions from the core diamagnetism, Landau diamagnetism, and Pauli paramagnetism. This can be expressed as

$$\chi_{dc} - \chi_{core} = S\,(\chi_{Landau} + \chi_{Pauli})\,, \qquad (1)$$

where S is the Stoner enhancement factor. This can be further simplified as

$$\chi_{dc} - \chi_{core} = S\,\chi_{Pauli}\left[1-\frac{1}{3}\left(\frac{m}{m_b}\right)\right], \qquad (2)$$

where $\chi_{Pauli} = n\,N_A\mu_B^2\,N(E_F)$ is the Pauli susceptibility, μ_B is the Bohr magneton, m is the free electron mass, and m_b is the band mass. Assuming the valence of La as 3, Rh as 3, and Si as 4, we estimate the core diamagnetism to be -2×10^{-4} emu/mol. We have also calculated the value of the Pauli susceptibility as 1.1×10^{-4} emu/mol, and this yields a value of 3.3 for the Stoner factor of $La_2Rh_3Si_5$.

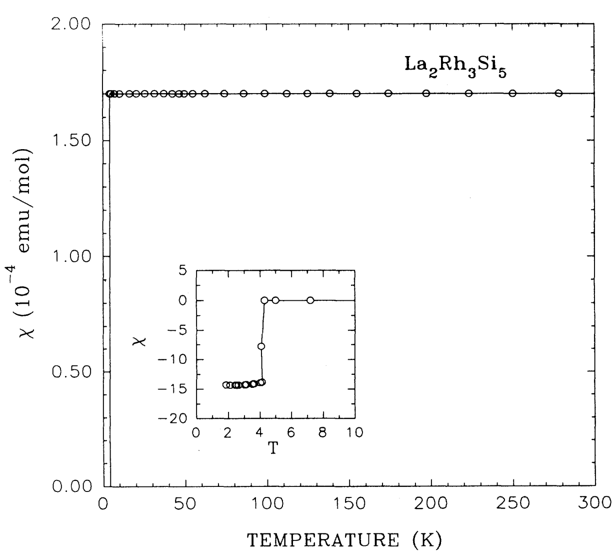

FIG. 2. Variation of susceptibility (χ) of $La_2Rh_3Si_5$ from 2 to 300 K. The inset shows the low-temperature ac χ data with the diamagnetic transition below 4.5 K.

2. Resistivity studies

The temperature dependence of the resistivity (ρ) of $La_2Rh_3Si_5$ is shown in Fig. 3. The inset shows the low-temperature ρ data on an expanded scale. The ρ data show a jump at 4.4 K, which is the superconducting transition temperature (T_c) of this sample. This is in accord with the T_c value obtained from χ data. In the normal state (5 K< T <25 K), the temperature dependence of ρ could be fitted to a power law, which can be written as

$$\rho = \rho_0 + a T^n. \tag{3}$$

The optimum value of n is found to be 3, and the values of ρ_0 and a are found to be 24.1 $\mu\Omega$ cm and 0.16 nΩ cm/K^3, respectively. This value of n agrees with the Wilson's s-d scattering model, which predicts a T^3 dependence of $\rho(T)$ for $T < \Theta_D/10$.

At high temperatures (100 K< T <300 K), the ρ data significantly deviates from the linear temperature dependence. Such a deviation from linear temperature dependence at high temperatures has been seen in many alloys, where the saturation is attributed to the high value of ρ of these alloys at these temperatures. This deviation from linearity occurs because the mean free path becomes short, of the order of few atomic spacings. When that happens, the scattering cross section will no longer be linear in the scattering perturbation. Since the dominant temperature-dependent scattering mechanism is the electron-phonon interaction here, the ρ will no longer be proportional to the mean-square atomic displacement, which is proportional to T for a harmonic potential. Instead, the resistance will rise less rapidly than linearly in T and will show negative curvature ($d^2\rho/dT < 0$). This behavior is also seen in previous studies on silicides and germanides.[16,17]

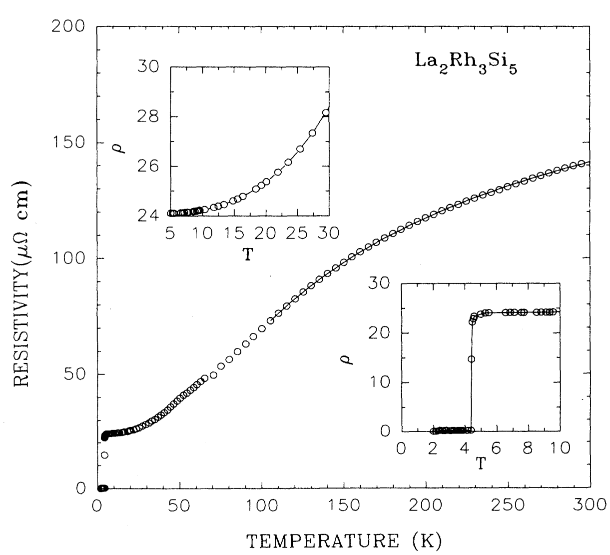

FIG. 3. Temperature dependence of resistivity (ρ) of $La_2Rh_3Si_5$ from 2 to 300 K. The insets show the low-temperature ρ data from 2 to 10 K and 5 to 30 K. The solid lines are fit to the models (see text).

One of the models that describe the $\rho(T)$ of these compounds is known as the parallel resistor model.[18] In this model the expression of $\rho(T)$ is given by

$$\frac{1}{\rho(T)} = \frac{1}{\rho_1(T)} + \frac{1}{\rho_{\max}} , \tag{4}$$

where $\rho_{\max}$ is the saturation resistivity, which is independent of temperature, and $\rho_1(T)$ is the ideal temperature-dependent resistivity. Further, the ideal resistivity is given by the expression

$$\rho_1(T) = \rho_0 + C_1\left(\frac{T}{\Theta_D}\right)^3 \times \int_0^{\Theta_D/T} \frac{x^3dx}{[1-\exp(-x)][\exp(x)-1]} , \tag{5}$$

where $\rho(0)$ is the residual resistivity, and the second term is due to phonon-assisted electron scattering similar to the s-d scattering in transition-metal alloys. Θ_D is the Debye temperature and C_1 is a numerical constant. Equation (4) can be derived if we assume that the electron mean free path l is replaced by $l + a$ (a being an average interatomic spacing). Such an assumption is reasonable, since infinitely strong scattering can only reduce the electron mean free path to a. Chakraborty and Allen[19] have made a detailed investigation of the effect of strong electron-phonon scattering within the framework of the Boltzmann transport equation. They find that the interband scattering opens up new "nonclassical channels," which account for the parallel resistor model. We found the value of $\rho_{\max}$ as 224.4 $\mu\Omega$ and that of Θ_D as 333 K by fitting the resistivity data to the above equations in the range 100 to 300 K.

3. Heat-capacity studies

The temperature dependence of the heat capacity (C_p) from 2 to 35 K of $La_2Rh_3Si_5$ is shown in Fig. 4. The inset shows the low-temperature C_p/T-vs-T data. The jump in C_p at 4.4 K (ΔC= 40 mJ/mol K) clearly shows bulk superconducting ordering in this sample below this temperature. The temperature dependence of C_p is fitted to the expression,

$$C_p = \gamma T + \beta T^3 , \tag{6}$$

where γ is due to electronic contribution and β is due to the lattice contribution. The value of the ratio $\Delta C_p/\gamma T_c$ is 0.56, which is significantly reduced from the BCS value of 1.43. Low values of $\Delta C_p/\gamma T_c$ have been observed before in the heat-capacity study of $R_2Fe_3Si_5$ compounds by Vining *et al.*[20] According to them, the reduced jump across T_c could arise from an extrinsic effect (such as inhomogeneity in the sample or magnetic impurities) or from an intrinsic effect (such as the existence of regions that do not participate in superconductivity). In our sample of $La_2Rh_3Si_5$, we estimate the impurity content to be less than 5% by volume and the sharpness of the superconducting transition also suggests good homogeneity. It is possible that the reduced jump could

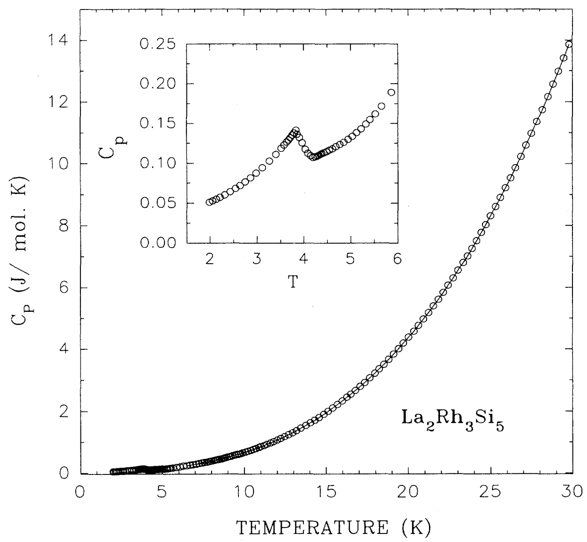

FIG. 4. Plot of C_p vs T of $La_2Rh_3Si_5$ from 1.9 to 30 K. The inset shows the same plot from 2 to 6 K to illustrate the bulk superconductivity.

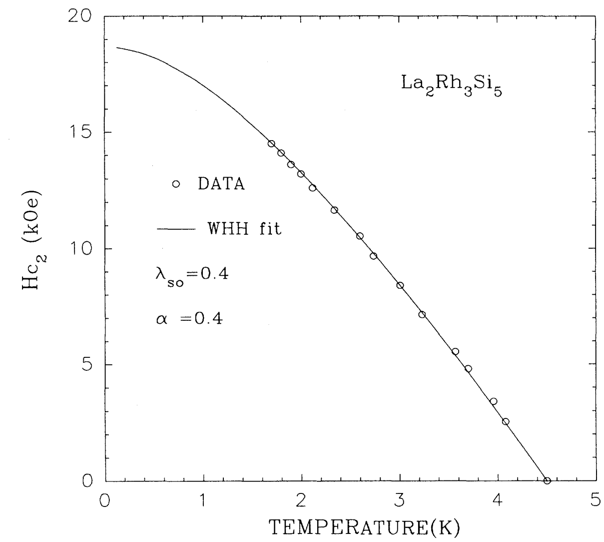

FIG. 5. Temperature dependence of the upper critical field (H_{c2}) of $La_2Rh_3Si_5$ from 1.7 to 4.45 K. The solid line is a fit to WHH theory for dirty type-II superconductors.

arise from two-band superconductivity where one band remains normal. However, detailed Fermi surface measurements are required before we can analyze the data in terms of this model. The fit to the heat-capacity data using Eq. (6) in the temperature range from 5 to 10 K yielded 16.3 mJ/mol K^2 and 0.5 mJ/mol K^4 for γ and β, respectively. The γ value has been obtained by matching the entropy of the normal and the superconducting states at T_c, as suggested by Stewart, Meisner, and Ku.[21] From the β value of 0.5 mJ/mol K^4, we estimate Θ_D to be 339 K using the relation

$$\Theta_D = \left(\frac{12\,\pi^4\,N\,r\,k_B}{5\beta}\right)^{1/3}, \qquad (7)$$

where N is Avogadro's number, r is the number of atoms per formula unit, and k_B is Boltzmann's constant.

4. *Upper-critical-field studies*

The estimation of the upper-critical-field (H_{c2}) value at a given temperature has been made by measuring the resistance of the sample under a given magnetic field. The transition temperature in a given field is defined as the temperature, which corresponds to the midpoint of the resistance jump. The temperature dependence of H_{c2} is shown in Fig. 5. It is well known that in nonmagnetic superconductors, the magnetic field interacts with the conduction electrons basically through two different mechanisms. Both lead to pair breaking and eventually destroy the superconductivity at a given field, which is known as the critical field. One of these mechanisms arises due to the interaction of the field with the orbital motion of the electrons (orbital pair breaking), and the other is due to the interaction of the field with the electronic spin (Pauli paramagnetic limiting effects). Orbital pair breaking is the dominant mechanism at low fields, and at very high fields, the Pauli paramagnetic effect limits the upper critical field. We have fitted this temperature dependence of H_{c2} to the theory of Werthamer, Helfand, and Hohenberg[22] (WHH), which incorporates a spin-orbit scattering term (λ_{so}) in dirty type-II superconducting materials. We obtain a value of 0.4 for λ_{so}, 23.0 kOe for $H_{c2}(0)$ and 7.5 kOe/K for dH_{c2}/dT near T_c. The value of the Pauli paramagnetic limiting field ($H_{\rm Pauli}$=18.4 T_c) for $La_2Rh_3Si_5$ is very large (81 kOe), compared to the estimated value of the upper critical field at 0 K. This could be the reason for the absence of Pauli paramagnetic limiting in the upper critical field of this compound. One can also estimate dH_{c2}/dT using the relation

$$dH_{c_2}/dT = 44.8\gamma\rho \text{ (in kOe/K)}, \qquad (8)$$

where γ is the electronic heat-capacity coefficient (ergs/cm^3 K^2) and ρ (Ω cm) is the residual resistivity. Substituting the values of γ and ρ, we get a value 1.6 kOe/K, which is only one fifth of the value obtained from the experiment. The reason for this large discrepancy is not understood at this moment, though similar anomalies in the value of dH_{c2}/dT have been reported in earlier studies.[23,24] In those earlier reports strongly coupled superconductors that have complex phonon spectra were studied. In that case, utilizing the WHH theory to analyze is not strictly valid, as the WHH theory assumes electron interaction via the weak-coupling BCS-type interaction potential and have a spherical Fermi surface.

B. Estimation of normal- and superconducting-state parameters

Using the value of Θ_D and T_c, we can estimate the electron-phonon scattering parameter λ from McMillan's theory,[25] where λ is given by

$$\lambda = \frac{1.04 + \mu^* \ln(\Theta_D/1.45\,T_c)}{(1-0.62\,\mu^*)\ln(\Theta_D/1.45\,T_c) - 1.04} . \quad (9)$$

Assuming $\mu^*=0.1$, we find the value of λ to be 0.53, which puts $La_2Rh_3Si_5$ as an intermediate coupling superconductor. On the basis of purely thermodynamical arguments, the thermodynamic critical field at T=0 K [$Hc(0)$] can be determined by integrating the entropy difference between the superconducting and normal states. From our experimental heat-capacity data, we obtain a value of 740 Oe for $Hc(0)$. One can also calculate the thermodynamical critical field $Hc(0)$ from the expression,[26]

$$Hc(0) = 4.23\gamma^{1/2}\,T_c , \quad (10)$$

where γ is the heat-capacity coefficient (erg/cm^3 K^2). This gives a value of $Hc(0)$ as 735 Oe. We can estimate the Ginzburg-Landau coherence length $\xi_{\rm GL}$ at $T = 0$ K from the relation

$$\xi_{\rm GL}(0) = \frac{8.57 \times 10^{-7}}{[\gamma\,\rho\,T_c]^{1/2}} , \quad (11)$$

where γ and ρ are the electronic heat-capacity coefficient (erg/cm^3 K^2) and the resistivity (Ωcm) of the sample just above T_c. This equation yields a value of 211 Å for $\xi_{\rm GL}(0)$.

Using the expression $\kappa(0) = 7.49 \times 10^3\,\gamma^{1/2}\,\rho$ [where $\kappa(0) = \lambda_{\rm GL}(0)/\xi_{\rm GL}(0)$], we get the $\kappa(0)$ value as 7.1. From the value of $\xi_{\rm GL}(0) = 211$ Å (determined earlier), we get a value of 1504 Å for the Ginzburg-Landau penetration depth $\lambda_{\rm GL}(0)$. The lower critical value can be determined by using the relation

$$Hc_1(0) = \frac{Hc\,(0)\,\ln[\kappa(0)]}{2^{1/2}\,\kappa(0)} , \quad (12)$$

which yields a value of 144 Oe for the lower critical field at 0 K. This value of $Hc_1(0)$ has to be verified with magnetization measurements on the same sample. Such measurements on this sample are in progress and will be reported elsewhere. The enhanced density of states can be calculated using the relation

$$N^*(E_F) = 0.2121\gamma/N , \quad (13)$$

where N is the number of atoms per formula unit and γ is expressed in mJ/mol K^2. The value of $N^*(E_F)$ is 0.34 states/(eV atom spin direction), and the value of the bare density of states $N(E_F) = N^*(E_F)/(1+\lambda) =$ 0.22 states/(eV atom spin direction).

The parameters are calculated using the Ginzburg-Landau theory for dirty superconductors. To verify the self-consistency of our approach, we have estimated the mean free path (l) of our sample using the expression

$$l = 1.27 \times 10^4\,[\rho\,n^{2/3}\,(S/S_F)]^{-1}, \quad (14)$$

where n is the conduction electron density in units of cm^{-3} and S/S_F is the ratio of the area of the Fermi surface to that of a free electron gas of density n. If one assumes a simple model of the spherical Fermi surface (S/S_F=1), the value of l would be 71 Å, and one can also calculate the value of the BCS coherence length (for S/S_F=1) from the expression

$$\xi_0 = 7.95 \times 10^{-17}\,[n^{2/3}]\,(\gamma\,T_c)^{-1} , \quad (15)$$

where γ is expressed in ergs/cm^3 K^2. The value of ξ_0 was found to be 862 Å, which is much higher than l, which implies $La_2Rh_3Si_5$ is a dirty type-II superconductor. Using the l value, ξ_0 can be compared with that obtained from the expression,

$$H^*_{c_2}(0) = \phi_0/4.54\,\xi_0\,l , \quad (16)$$

where $H^*_{c_2}(0)$ is the orbital critical field, which is given by the relation

$$H^*_{c_2}(0) = 3.06 \times 10^4\,\rho\,\gamma\,T_c. \quad (17)$$

Substituting the value of $H^*_{c_2}(0)$ obtained from Eq. (17) in Eq. (16), we get a value of 1269 Å for ξ_0. The difference in the estimated value of ξ_0 obtained from Eqs. (15) and (16) is a large value of the extrapolated $H_{c2}(0)$ from the experiment (23.4 kOe) compared to the estimated critical field value (5.06 kOe). The normal- and superconducting-state parameters are listed in Table I.

C. Study of antiferromagnetism in $Nd_2Rh_3Si_5$

1. *Magnetic susceptibility studies*

The temperature dependence of the inverse dc magnetic susceptibility ($1/\chi_{\rm dc}$) of the $Nd_2Rh_3Si_5$ sample in a field of 4 kOe from 2 to 300 K is shown in Fig. 6. The inset shows the inverse ac susceptibility behavior of the same sample at low temperature in an ac field of 2 Oe. This inset clearly shows the antiferromagnetic ordering of Nd spins below 2.7 K. A previous study[14] indicated that antiferromagnetism is possible in a well-

TABLE I. Superconducting and normal-state properties of $La_2Rh_3Si_5$.

Parameter	Units	Value
T_C	K	4.45
γ	mJ/mol K^2	16.3
β	mJ/mol K^4	0.50
Θ_D	K	339
λ		0.53
$N^{\rm a}(E_F)$	states/(eV atom spin)	0.34
$N(E_F)$	states/(eV atom spin)	0.22
$\xi_{\rm GL}(0)$	Å	211
$\lambda_{\rm GL}(0)$	Å	1504
$Hc_2(0)$	kOe	23
$Hc_1(0)$	Oe	144
$Hc(0)$	Oe	735
l	Å	71
$\xi_0^{\rm BCS}$	Å	862
ξ_0	Å	1269[a]
S		3.1

[a] Estimated from the Eq. (16).

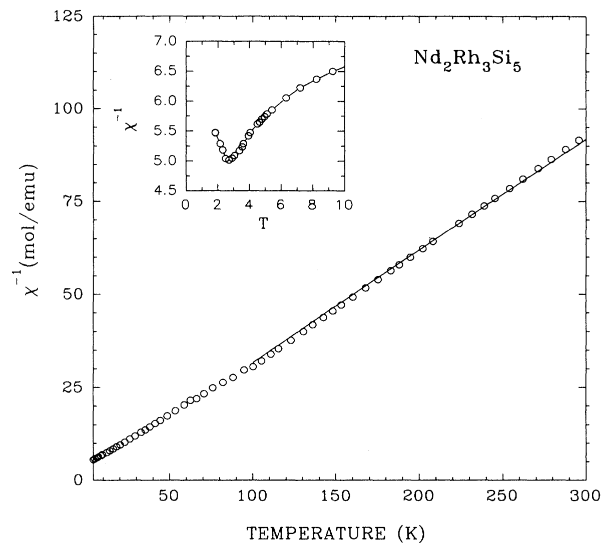

FIG. 6. Variation of inverse susceptibility $(1/\chi)$ of $Nd_2Rh_3Si_5$ from 2 to 300 K. The inset shows the low-temperature $1/\chi$ data with a slope change around 2.7 K.

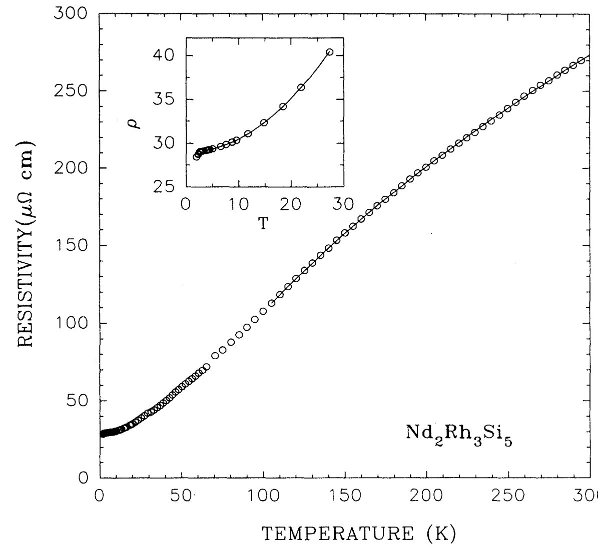

FIG. 7. Temperature dependence of resistivity (ρ) of $Nd_2Rh_3Si_5$ from 2 to 300 K. The inset shows the low-temperature ρ data from 2 to 30 K. A small kink in ρ near 2.7 K in the inset indicates antiferromagnetic ordering in this compound. The solid lines are fit to the models (see text).

characterized sample of $Nd_2Rh_3Si_5$. However, that paper did not report the actual antiferromagnetic ordering temperature in this sample. In this compound the Nd-Nd distance is estimated to be of the order of 4 Å. It is possible that the Rudermann-Kittel-Kasuya-Yosida (RKKY) interaction between the Nd^{3+} ions is responsible for the low-temperature ordering of Nd spins. However, at these low temperatures, there is also a possibility that the dipole-dipole interactions can also contribute to the observed antiferromagnetism.

The high-temperature susceptibility (100 K $< T <$ 300 K) is fitted to a modified Curie-Weiss expression, which is given by

$$\chi = \chi_0 + \frac{C}{(T - \Theta_p)} , \tag{18}$$

where C is the Curie constant, which can be written in terms of the effective moment as

$$C = \frac{\mu_{\rm eff}^2 \, x}{8} , \tag{19}$$

where x is the concentration of Nd ions (x to 2 for $Nd_2Rh_3Si_5$). The values of χ_0, C, and Θ_p are found to be -1.005×10^{-4}, 3.4, and -8.97, respectively. The estimated effective moment is found to be around $3.69\mu_B$, which is slightly larger than the free-ion moment of the Nd^{3+} ion ($3.62\mu_B$). This implies a contribution from the conduction electrons (from the Rh band) to the Nd magnetic moment. Below 100 K, the χ data show deviation from the Curie-Weiss plot, which could be due to the presence of crystal-field contributions.

2. Resistivity studies

The temperature dependence of the resistivity (ρ) of $Nd_2Rh_3Si_5$ is shown in Fig. 7. The inset shows the low-temperature ρ data on an expanded scale. The ρ data show a kink at 2.7 K, which is the antiferromagnetic ordering temperature (T_n) of this sample. This is in accord with the T_n value obtained from the χ data. In the temperature range 5 K$< T <$ 25 K, the temperature dependence of ρ could be fitted to a T^2 dependence in contrast to the T^3 dependence observed in $La_2Rh_3Si_5$. At high temperatures, the ρ behavior is similar to that observed in $La_2Rh_3Si_5$, and the data could be fitted to the parallel resistor model.

D. Heat-capacity studies on $Nd_2Rh_3Si_5$

The temperature dependence of C_p from 2 to 35 K of $Nd_2Rh_3Si_5$ is shown in Fig. 8. The inset shows the low-temperature C_p data. The large jump at 2.6 K ($\Delta C=$ 6.1 J/mol K) clearly shows bulk magnetic ordering in this sample. This temperature is slightly lower than the T_n value observed from the χ as well ρ measurements. From these observations, we conclude that this sample undergoes antiferromagnetic ordering below 2.7 K. The magnetic contribution to the heat-capacity (which is obtained after subtracting the measured C_p data from that of $La_2Rh_3Si_5$) is shown in Fig. 9. The calculated entropy is also shown in the same figure. The increase in the entropy at high temperatures ($T >$20 K) signifies contribution from crystal-field effects in this sample. The total entropy below T_n is found to be 2.7 J/mol K, which is significantly less than the value of R ln2 (entropy for the magnetic doublet), and this shows the existence of antiferromagntic correlations above T_n. Preliminary calculations suggest that the next excited state is also a doublet, and its separation from this doublet ground

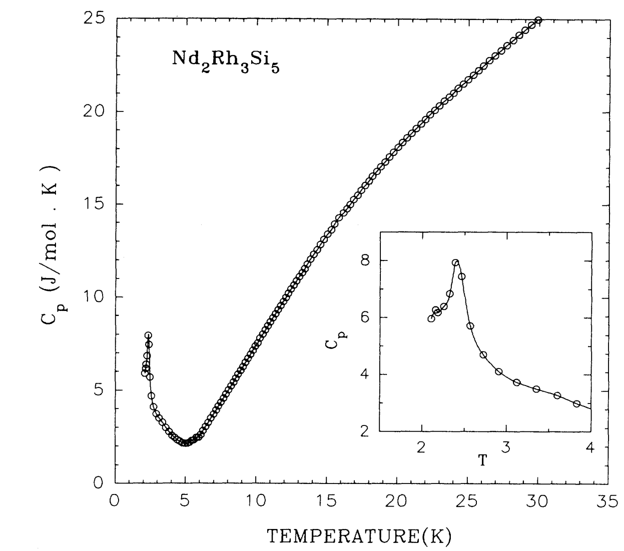

FIG. 8. Plot of C_p vs T of $Nd_2Rh_3Si_5$ from 2 to 35 K. The inset shows the same plot from 2 to 4 K. A large jump of 4 J/mol K signifies bulk magnetic ordering of Nd^{3+} spins.

state is approximately 42 K. Exact calculation of the crystal-field contribution to the heat-capacity, susceptibility, and resistivity requires a detailed model, which is in progress and will be published elsewhere. From the high-temperature heat-capacity data, we estimate the Debye temperature for this sample to 320 K, which agrees with the result obtained from the resistivity analysis.

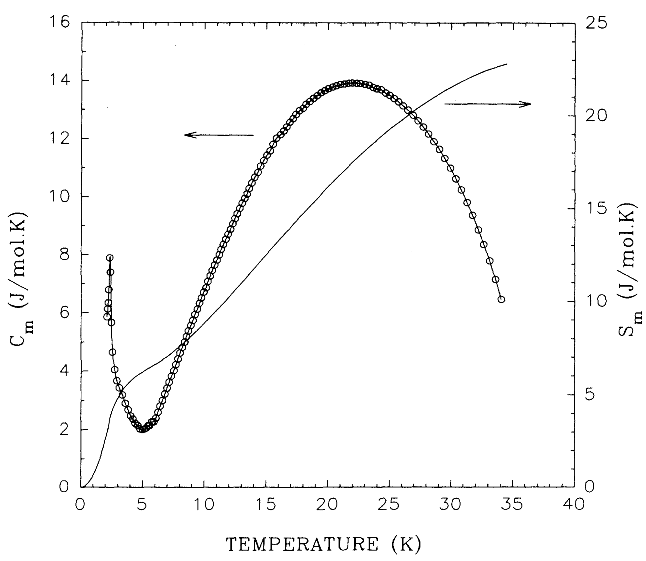

FIG. 9. Plot of magnetic contribution to the heat-capacity (C_m) vs T of $Nd_2Rh_3Si_5$ from 2 to 35 K. The solid line is the magnetic contribution to the entropy (S). The value of the entropy below T_n is $\approx$2.7 J/mol K which implies the existence of strong antiferromagnetic correlations above T_n.

E. Normal-state properties of $La_{2-x}Nd_xRh_3Si_5$

1. Magnetic susceptibility studies

The temperature dependence of the inverse susceptibility ($1/\chi$) for $La_{2-x}Nd_xRh_3Si_5$ for $x \leq 0.5$ and $x \geq 1$ are shown in Figs. 10 and 11, respectively. The temperature dependence of χ data from 100 to 300 K can be fitted to the Curie-Weiss relation given by Eq. (17). The values of Θ_p, μ_{eff}, and x are given in Table II. The effective magnetic moments are found to vary from 3.7 μ_B (for x =2) to 4.1μ_B (for x=0.2) in this series. The large values of μ_{eff} (compared to the free-ion value 3.62μ_B of the Nd^{3+} ion) are attributed to the conduction electron contribution in the pseudoternary alloys. The value of Θ_p also increases as x decreases from 2 to 0.2. Below 100 K, the temperature dependence of $1/\chi$ deviates from linearity, which could be because of crystal-field effects.

2. Resistivity studies

The low-temperature dependence of resistivity (ρ) for $La_{2-x}Nd_xRh_3Si_5$ for $x \leq 1$ and $x \geq 1$ are shown in Figs. 12 and 13, respectively. The high-temperature data are shown in Figs. 14 and 15, respectively. The resistivity data of $La_{2-x}Nd_xRh_3Si_5$ show power-law behavior at low temperature and deviation from linear temperature dependence at high temperatures, as we have seen in the the $La_2Rh_3Si_5$ and $Nd_2Rh_3Si_5$ samples. The resistivity data at low temperatures show power-law dependence [see Eq.(2)] with n=3.0 for x=0.0, and it decreases to 1.5 in the intermediate concentrations and finally changes to 2 for antiferromagnetic $Nd_2Rh_3Si_5$ (x=2). The pa-

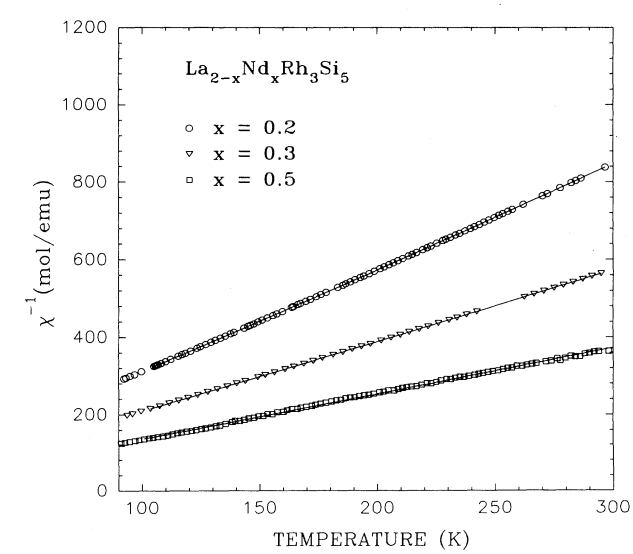

FIG. 10. Variation of the inverse dc susceptibility ($1/\chi$) of $La_{2-x}Nd_xRh_3Si_5$ for ($x \leq 0.5$) from 100 to 300 K in a field of 4 kOe. The solid lines are fit to the Curie-Weiss relation (see text for details).

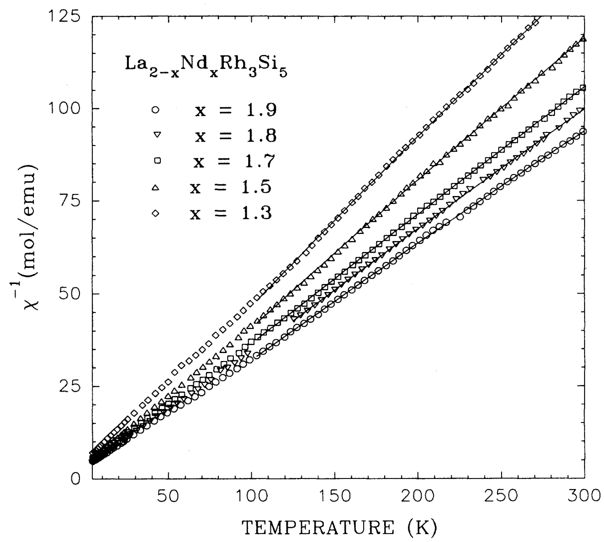

FIG. 11. Variation of inverse dc susceptibility ($1/\chi$) of $La_{2-x}Nd_xRh_3Si_5$ for ($x \geq 1.0$) from 4 to 300 K in a field of 5 kOe. The solid lines are fit to the Curie-Weiss relation (see text for details).

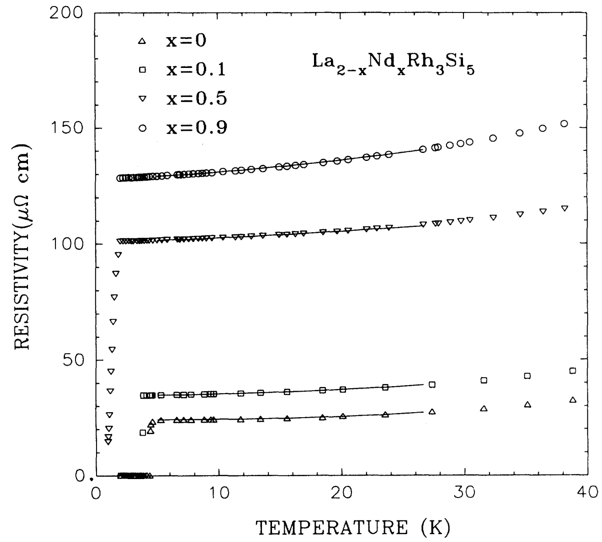

FIG. 12. Low-temperature dependence of resistivity (ρ) of $La_{2-x}Nd_xRh_3Si_5$ ($x \leq 1.0$) from 2 to 40 K. The sharp drop in ρ in $x = 0$, 0.1, and 0.5 is due to the superconducting transition of the respective samples. The solid lines are fit to the power-law expression (see text).

rameters obtained from the analysis of low-temperature resistivity data are given in Table III.

The high-temperature data could be fitted to the parallel resistor model. The solid lines correspond to the fit to the parallel resistor model from 100 to 300 K. The value of ρ_{max} is found to vary from 224 $\mu\Omega$ cm to 1.6 mΩ cm, whereas the Θ_D value obtained is found to lie between 167 and 332 K. The saturation resistivity (ρ_{max}) is found to have the maximum value for alloys having intermediate concentrations. For these alloys, the residual resistivity also have the maximum value indicating the presence of strong disorder. The values of the parameters obtained from the fit to the parallel resistor model are given in Table IV.

F. Superconductivity and antiferromagnetism in $La_{2-x}Nd_xRh_3Si_5$

1. *Superconductivity of $La_{2-x}Nd_xRh_3Si_5$*

The T_c dependence on the Nd concentration in $La_{2-x}Nd_xRh_3Si_5$ is shown in Fig. 16. In this case, the

TABLE II. Magnetic properties of $La_{2-x}Nd_xRh_3Si_5$.

Sample	C	μ_{eff}	Θ_p
$Nd_2Rh_3Si_5$	3.4	3.69 μ_B	−8.9 K
$La_{0.1}Nd_{1.9}Rh_3Si_5$	3.28	3.71 μ_B	−8.7 K
$La_{0.2}Nd_{1.8}Rh_3Si_5$	3.11	3.72 μ_B	−7.6 K
$La_{0.3}Nd_{1.7}Rh_3Si_5$	2.94	3.72 μ_B	−7.5 K
$La_{0.5}Nd_{1.5}Rh_3Si_5$	2.60	3.72 μ_B	−7.2 K
$La_{0.7}Nd_{1.3}Rh_3Si_5$	2.27	3.73 μ_B	−7.2 K
$La_{1.5}Nd_{0.5}Rh_3Si_5$	0.86	3.74 μ_B	−14.9 K
$La_{1.7}Nd_{0.3}Rh_3Si_5$	0.58	3.93 μ_B	−17.7 K
$La_{1.8}Nd_{0.2}Rh_3Si_5$	0.42	3.41 μ_B	−28.1 K

T_c depression can be expressed in terms of the magnetic pair-breaking theory of Abrikosov and Gor'kov (AG),[27] which is given by the equation,[28]

$$\ln(T_0/T_{c0}) = \psi(0.5) - \psi(0.5+\Gamma) , \quad (20)$$

where ψ is the digamma function and Γ is the pair-breaking parameter, which is given by

$$\Gamma = 0.14\,(\alpha/\alpha_{cr})\,(T_{c0}/T_c) = 0.14\,(n/n_{cr})\,(T_{c0}/T_c) , \quad (21)$$

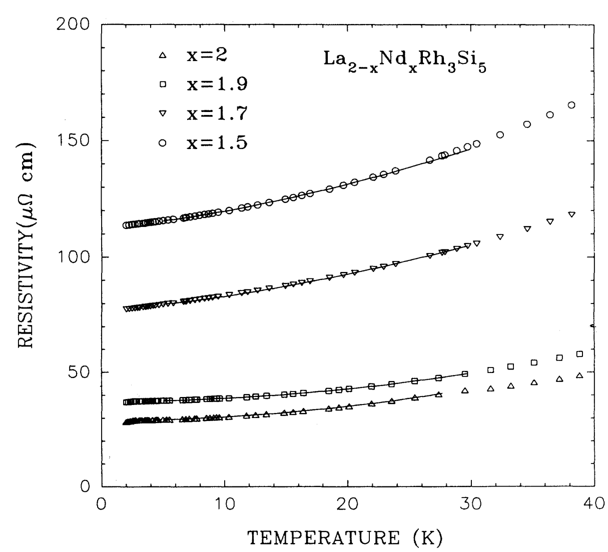

FIG. 13. Low-temperature dependence of resistivity (ρ) of $La_{2-x}Nd_xRh_3Si_5$ ($x \geq 1.0$) from 2 to 40 K. The solid lines are fit to the power-law expression (see text).

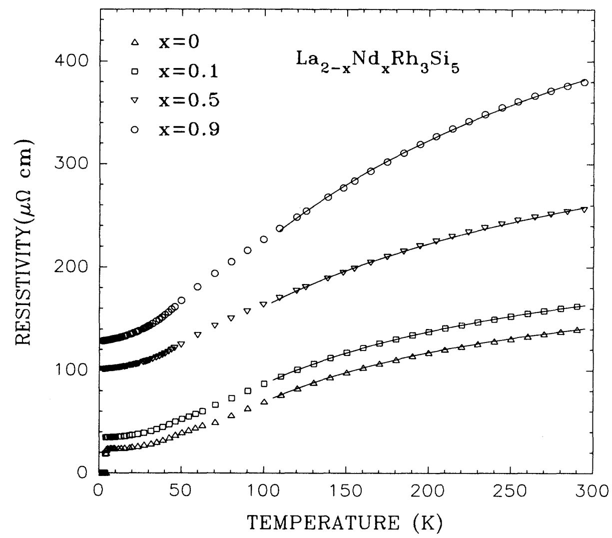

FIG. 14. The temperature dependence of resistivity (ρ) of $La_{2-x}Nd_xRh_3Si_5$ ($x \leq 1.0$) from 2 to 300 K. The solid lines are fit to the parallel resistor model (see text).

where n_{cr} is given by

$$n_{cr} = \frac{k_B T_{c0}}{4\gamma_E\ N(0)\ J_{sf}^2\ (g_J - 1)^2\ J(J+1)}\ , \qquad (22)$$

where γ_E is the Euler's constant, $N(0)$ is the density of states of the parent compound, and J_{sf} is the interaction parameter between conduction electrons and the rare-earth spin. In the limit $n \to 0$, the rate of decrease of T_c with Nd concentration x can be written as

$$\frac{dT_c}{dn} = 5\ \frac{dT_c}{dx} = -(\pi^2/2)\ N(0)\ k_B^{-1}\ J_{sf}^2\ (g_J - 1)^2 \times J(J+1). \qquad (23)$$

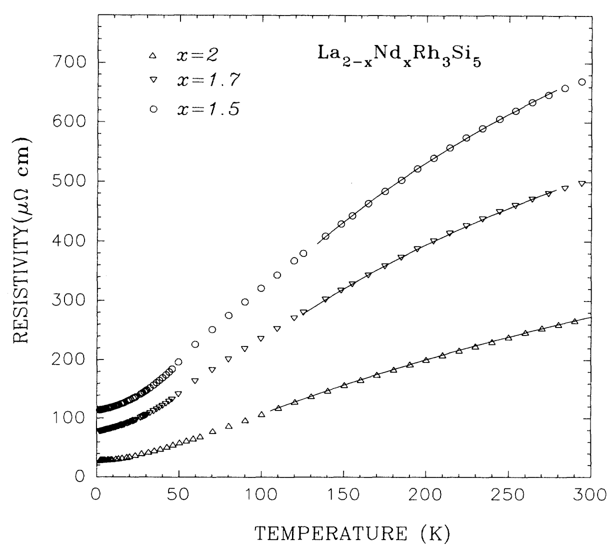

FIG. 15. The temperature dependence of resistivity (ρ) of $La_{2-x}Nd_xRh_3Si_5$ ($x \geq 1.0$) from 2 to 300 K. The solid lines are fit to the parallel resistor model (see text).

TABLE III. Parameters obtained from the low-temperature resistivity fit of $La_{2-x}Nd_xRh_3Si_5$.

Sample	ρ_0 ($\mu\Omega$ cm)	a ($\mu\Omega$/ K^n)	n
$Nd_2Rh_3Si_5$	28.95	0.0154	2.0
$La_{0.1}Nd_{1.9}Rh_3Si_5$	37.21	0.0137	2.0
$La_{0.3}Nd_{1.7}Rh_3Si_5$	77.86	0.165	1.5
$La_{0.5}Nd_{1.5}Rh_3Si_5$	113.3	0.201	1.5
$La_{1.1}Nd_{0.9}Rh_3Si_5$	128.1	0.089	1.5
$La_{1.5}Nd_{0.5}Rh_3Si_5$	100.9	0.047	1.5
$La_{1.9}Nd_{0.1}Rh_3Si_5$	34.58	0.0062	2.0
$La_2Rh_3Si_5$	24.11	0.00016	3.0

Assuming the values of J=9/2, g_J=8/11, $N(0)$=0.34, and dT_c/dx= 0.06 K/at % of Nd, we estimate the value of J_{sf} as 29 meV. The dotted line in the Fig. 16 is a fit to the AG theory, and the critical concentration ($n_{cr} = x_{cr}/5$) is found to be 0.102. the quality of this fit is poor, since we did not consider the contribution from the crystal-field effects. The T_c-vs-x data could also be fitted by taking the crystal-field effects into consideration using the formalism proposed by Fulde and Peschel.[29] The energy separation of the first excited state from the ground state is estimated to be 42 K from the analysis of the Schottky anomaly observed in the heat-capacity data. Using this value, we get a value of 37 meV for J_{sf} from this fit. One can clearly see that the quality of this fit is very good compared to that of simple AG theory. The value of J_{sf} is large compared to those obtained by others in rare-earth intermetallic borides and stannides.[30,31] Such a value of J_{sf} is sufficient to suppress the coexistence of superconductivity and antiferromagnetism in $La_{2-x}Nd_xRh_3Si_5$ above 0.6 K. Measurements below 0.6 K might reveal the existence of coexistence region in this system.

In general, introduction of magnetic atoms in a superconductor decreases its transition temperature due to strong pair breaking. This pair breaking arises because of the exchange interaction of the conduction electrons with the localized magnetic moment. However, in the case of chalcogenides and rhodium borides,[32,33] the exchange interaction between the conduction electrons and the localized magnetic moments is small, and it is of the order $J_{sf} \approx$0.01 eV.[34] The small magnitude of J_{sf} enables both RRh_4B_4 and RMo_6S_8 compounds to retain their superconductivity, even in the presence of a relatively large concentration of rare-earth magnetic moments, which re-

TABLE IV. Parameters obtained from the parallel resistor model fit in $La_{2-x}Nd_xRh_3Si_5$.

Sample	ρ_{max}	ρ_1	C	Θ_D
$Nd_2Rh_3Si_5$	1010	25.46	592.9	247.5
$La_{0.1}Nd_{1.9}Rh_3Si_5$	754.9	13.98	490.13	167.32
$La_{0.3}Nd_{1.7}Rh_3Si_5$	1249.3	74.67	1430	265.25
$La_{0.5}Nd_{1.5}Rh_3Si_5$	1649.4	118.1	2105.7	289.64
$La_{1.1}Nd_{0.9}Rh_3Si_5$	646.28	84.78	1331	238.5
$La_{1.5}Nd_{0.5}Rh_3Si_5$	260.28	17.72	785.8	266.7
$La_{1.9}Nd_{0.1}Rh_3Si_5$	261	30.38	907.29	315.0
$La_2Rh_3Si_5$	224.34	14.1016	850.56	332.56

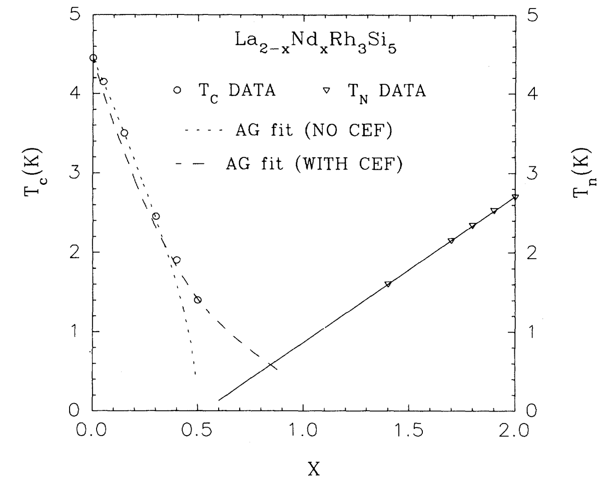

FIG. 16. The dependence of the superconducting transition temperature (T_c) and the antiferromagnetic ordering temperature (T_n) of $La_{2-x}Nd_xRh_3Si_5$ on the Nd concentration (x). The dotted line is a fit to the AG theory without crystal-field contributions and the dashed line represents a fit with AG theory including crystal-field effects. The solid line is a guide to the eye.

sults in magnetic ordering via indirect RKKY interaction at low temperatures. The reason for the small value of the exchange interaction lies in the structure of these compounds. For instance, in the case of RMo_6S_8,[32] the rare-earth atom occupies the first site at the rhombohedral cell, and therefore they are situated far away from Mo atoms, which results in weak d-f exchange. In the $La_{2-x}Nd_xRh_3Si_5$ system, although Nd-Nd separation is large, (>4 Å), the value of J_{sf} is also large, which probably prevents the coexistence of antiferromagnetism and superconductivity above 0.6 K. However, the crystal-field effects sufficiently weaken the T_c dependence on x so that coexistence is possible in this system below 0.6 K. In the case of the $R_2Fe_3Si_5$ system, Segre *et al.*[1] have made preliminary studies to look for coexistence of antiferromagnetism and superconductivity. He has found that in the $Lu_{2-x}Er_xFe_3Si_5$ and $Y_{2-x}Dy_xFe_3Si_5$ series such a coexistence is possible below 1.0 K and 0.5 K respectively. In this sense, our studies in $R_2Rh_3Si_5$ show a similarity with that of the $R_2Fe_3Si_5$ system, although the latter system does not form with light rare-earth elements.

2. *Upper-critical-field studies in* $La_{2-x}Nd_xRh_3Si_5$

The temperature dependence of the upper critical field for x=0.1 and 0.2 is shown in Figs. 17 and 18, respectively. Figs. 3 and 18. We have fitted these data using WHH theory with the additional pair-breaking parameter λ_m. We have used the relation given by Fisher and co-workers[35,36] which can be written as

$$\ln(t) = \psi[0.5] - (0.5 + iX)\,\psi\left(0.5 + \frac{(H1 + i\gamma)}{(2t)}\right) - (0.5 - iX)\,\psi\left(0.5 + \frac{(H1 - i\gamma)}{(2t)}\right), \quad (24)$$

where $i = \sqrt{-1}$, $t = T/T_c$, and γ, X, and $H1$ are given by the equations

$$\gamma = [(\alpha^2\,(H1 + H_j)^2 - 0.25(\lambda_{so} - \lambda_m)^2]^{1/2}, \quad (25)$$

$$X = (\lambda_{so} - \lambda_m)0.25, \quad (26)$$

$$H1 = H_r + 0.25(\lambda_{so} - \lambda_m), \quad (27)$$

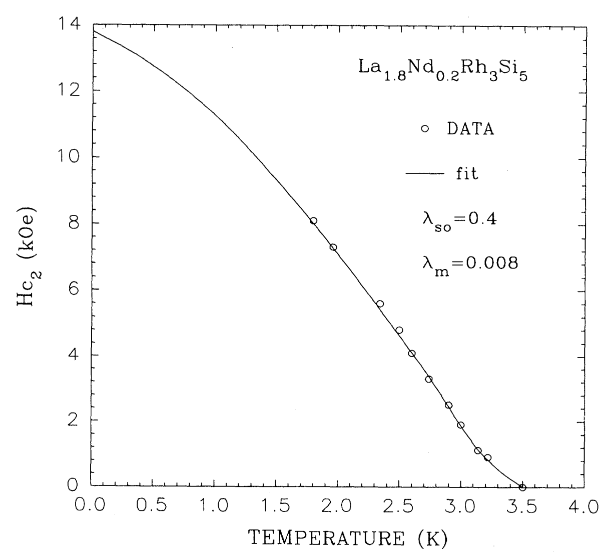

FIG. 17. Temperature dependence of the upper critical field (H_{c2}) of $La_{1.8}Nd_{0.2}Rh_3Si_5$ from 1.7 to 4.45 K. The solid line is a fit to WHH theory for dirty type-II superconductors with an additional magnetic pair-breaking parameter.

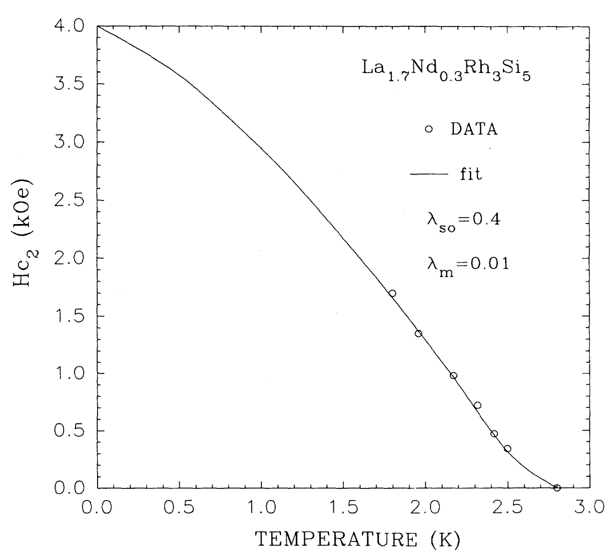

FIG. 18. Temperature dependence of the upper critical field (H_{c2}) of $La_{1.7}Nd_{0.3}Rh_3Si_5$ from 1.7 to 4.45 K. The solid line is a fit to WHH theory for dirty type-II superconductors with an additional magnetic pair-breaking parameter.

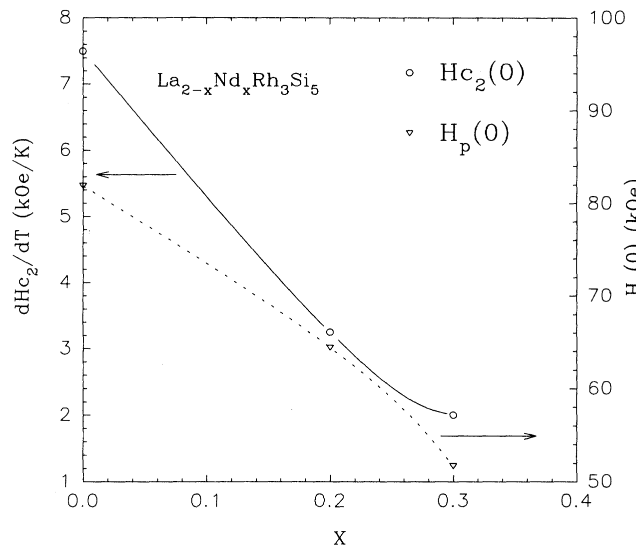

FIG. 19. The variation of the slope of the upper critical field (dH_{c2}/dT) near T_c and the Pauli limiting field [$H_p(0)$] of $La_{2-x}Nd_xRh_3Si_5$ with x.

where α is the Maki parameter, λ_{so} and λ_m are spin-orbit scattering and additional pair-breaking parameters, and H_r and H_j are reduced and exchange fields. Equation (24) reduces to the WHH result when λ_m=0.0. We have used λ_{so}=0.4, which has been obtained from the WHH fit to the H_{c2} dependence in $La_2Rh_3Si_5$. The dependence of dH_{c2}/dT and H_p (Pauli limiting field) with the concentration x is shown in Fig. 19.

3. Antiferromagnetism in $La_{2-x}Nd_xRh_3Si_5$

The T_c dependence on the Nd concentration in $La_{2-x}Nd_xRh_3Si_5$ is also shown in Fig. 16. The antiferromagnetic ordering temperature decreases linearly with La substitution as x decreases. A similar reduction in T_n vs nonmagnetic rare-earth substitution has been observed in other systems as well.[31] If one assumes the Nd spins interact via RKKY interaction, the magnetic transition temperature in the mean-field approximation is given by the expression[32]

$$k_B\, T_n \;=\; z\,(J')^2\,(g_J-1)^2\,J(J+1)\,, \tag{28}$$

where z is the average number of near-neighbor magnetic atoms. For the $La_{2-x}Nd_xRh_3Si_5$ system, z = 4 and $(J')^2 \approx N(0)\,J_{sf}^2$. Since $T_n \propto z$, the dilution of Nd by La in $La_{2-x}Nd_xRh_3Si_5$ shows a decrease of T_n with x. We have estimated the value of J' as 5.6 meV, which is much smaller than the J_{sf} value (37 meV). To an order of magnitude, the parameters J' and J_{sf} are related by

$$|J_{sf}| \;=\; J'/[N(E_F)]^{1/2}. \tag{29}$$

Using the values of J' and $N(E_F)$, we get a value J_{sf} as 3.9 meV, which suggests that the exchange coupling of the conduction electrons to the rare-earth magnetic moments is strong enough to mediate the indirect exchange interaction. Similar conclusions were drawn in an earlier study of RRh_4B_4 systems by McKay *et al.*[30]

IV. CONCLUSION

We have shown the existence of bulk superconductivity in $La_2Rh_3Si_5$ at 4.45 K and bulk antiferromagnetic ordering in $Nd_2Rh_3Si_5$ below 2.7 K. We find no region of coexistence of antiferromagnetism and superconductivity in the $La_{2-x}Nd_xRh_3Si_5$ system above 0.6 K. Similar behavior was observed by Segre *et al.* in the $R_{2-x}R'_xFe_3Si_5$ system (where R and R' are nonmagnetic and magnetic rare-earth elements, respectively).[1] Although T_c vs x could not be fitted to normal AG theory, we could get a good fit by incorporating crystal-field effects in AG theory as suggested by Fulde *et al.* We have suggested that the large value of J_{sf} (37 meV) prevents the coexistence of antiferromagnetism and superconductivity above 0.6 K. The upper critical field with x=0 was fitted to the WHH theory, and for finite values of x we have used Fisher's modification of the WHH equation[35] for superconductors doped with magnetic impurities.

[1] P. Rogl, in *Handbook of Physics and Chemistry of Rare Earths*, edited by K.A. Gschneidner, Jr. and L. Eyring (Elsevier Science Publishers, North-Holland, Amsterdam, 1984), Vol. 7, pp. 1–264.

[2] J. Leciejewicz and A. Szytula, in *Handbook of Physics and Chemistry of Rare Earths* (Ref. 1) Vol. 12, p. 133.

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

[4] R.N. Shelton, in *Proceedings of the International Conference on Superconductivity in d- and f- Band Metals, Karlsruhe, 1982*, edited by W. Buckel and W. Weber (Kernforshungszentrum, Karlsruhe, Germany, 1982), p. 123.

[5] H.F. Braun, Phys. Lett. **75A**, 386 (1980).

[6] H.F. Braun, C.U. Segre, F. Acker, M. Rosenberg, S. Dey, and U. Deppe, J. Magn. Magn. Mater. **25**, 117 (1981).

[7] A.R. Moodenbaugh, D.E. Cox, and H.F. Braun, Phys. Rev. B **25**, 4702 (1981).

[8] C.B. Vining and R.N. Shelton, Phys. Rev. B **28**, 2732 (1983).

[9] H.F. Braun in *Ternary Superconductors*, edited by G.K. Shenoy, B.D. Dunlap, and F.Y. Fradin (North-Holland, Amsterdam, 1980), p. 225.

[10] J.A. Gotaas, J.W. Lynn, R.N. Shelton, P. Klavins, and H.F. Braun, Phys. Rev. B **36**, 7277 (1987).

[11] S. Noguchi and K. Okuda, Physica B **194-196**, 1975 (1994).

[12] B. Chevalier, P. Lejay, J. Etourneau, M. Vlasse, and P. Hagenmuller, Mater. Res. Bull. **17**, 1211 (1980).

[13] P. Lejay, I. Higashi, B. Chevalier, J. Etourneau, and P. Hagenmuller, Mater. Res. Bull. **19**, 115 (1984).

[14] G. Venturini, M. Meot-Meyer, J.F. Mareche, B. Malaman, and B. Roques, Mater. Res. Bull. **21**, 33 (1986).
[15] S. Ramakrishnan, S. Sundaram, R. S. Pandit, and Girish Chandra, J. Phys. E **18**, 650 (1985).
[16] S. Ramakrishnan, K. Ghosh, and Girish Chandra, Phys. Rev. B **45**, 10 769 (1992).
[17] K. Ghosh, S. Ramakrishnan, and Girish Chandra, Phys. Rev. B **48**, 10 440 (1993).
[18] H. Wiesmann, M. Gurvitch, H. Lutz, A.K. Ghosh, B. Schwarz, M. Strongin, P.B. Allen, and J.W. Halley, Phys. Rev. Lett. **38**, 782 (1977).
[19] B. Chakraborty and P.B. Allen, Phys. Rev. Lett. **38**, 372 (1979).
[20] C.B. Vining, R.N. Shelton, H.F. Braun, and M. Pelizzone, Phys. Rev. B **27**, 2800 (1983).
[21] G.R. Stewart, G. P. Meisner, and H. C. Ku in *Proceedings of the IVth International Conference in d- and f- Band Superconductivity, Karlsruhe, 1982*, edited by W. Buckel and W. Weber (Kernforschungszentrum, Karlsruhe, 1982), p. 81.
[22] N.R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. **147**, 295 (1966).
[23] L.S. Hauermann and R.N. Shelton, Phys. Rev. B **35**, 4673 (1987).
[24] W.H. Lee, S. Appl, and R. Shelton, J. Low Temp. Phys. **68**, 147 (1987).
[25] W.L. McMillan, Phys. Rev. **167**, 331 (1967).
[26] T.P. Orlando, E.J. McNiff, Jr., S. Foner, and M.R. Beasley, Phys. Rev. B **19**, 4545 (1979).
[27] A.A. Abrikosov and L.P. Gor'kov, Sov. Phys. JETP **12**, 1243 (1961).
[28] For an excellent review on the effect of magnetic impurities on the superconductivity of metallic alloys, see M.B. Maple, J. Appl. Phys. **9**, 179 (1976).
[29] P. Fulde and I. Peschel, Adv. Phys. **21**, 1 (1972)
[30] H.B. MacKay, L.D. Woolf, M.B. Maple, and D.C. Johnston, J. Low. Temp. Phys. **41**, 639 (1980).
[31] S.K. Malik, A.M. Umarji, and G.K. Shenoy, Phys. Rev. B **32**, 4426 (1985).
[32] O. Pena and M. Sergent, Prog. Solid State Chem. **19**, 165 (1989).
[33] O. Fisher in *Ferromagnetic Materials*, edited by K.H.J. Buschow and E.P. Wohlfarth (Elsevier, Holland, 1990), Chap. 6.
[34] See the papers in *Superconductivity in Ternary Compounds*, edited by M.B. Maple and O. Fisher (Springer-Verlag, Berlin, 1984), Vol. II.
[35] O. Fisher, Helv. Acta Phys. **45**, 331 (1972).
[36] O. Fisher, M. Ishikawa, M. Pelizzone, and A. Teyvaud, J. Phys. (Paris) Collog. **40**, C5-89 (1979).