Type-I superconductivity in $ScGa_3$ and $LuGa_3$ single crystals

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We present evidence of type-I superconductivity in single crystals of $ScGa_3$ and $LuGa_3$, from magnetization, specific heat, and resistivity measurements: low critical temperatures $T_c = 2.1$–2.2 K; field-induced second- to first-order phase transition in the specific heat, critical fields less than 240 Oe; and low Ginzburg-Landau coefficients $\kappa \approx 0.23$ and 0.30 for $ScGa_3$ and $LuGa_3$, respectively, are all traits of a type-I superconducting ground state. These observations render $ScGa_3$ and $LuGa_3$ two of only several type-I superconducting compounds, with most other superconductors being type II (compounds and alloys) or type I (elemental metals and metaloids).

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I. INTRODUCTION

Despite the large number of known conventional and unconventional superconductors (SCs), new findings still emerge even from simple, binary intermetallic systems. The majority of the metallic elements are superconducting with small values of the critical temperatures T_c.[1] It has been noted[2] that intermetallic compounds often have T_c values higher than those of the constituent elements, as is the case in Nb_3Sn,[3] V_3Si,[4] ZrB_2, and NbB_2.[5] In this work, we present thermodynamic and transport measurements on single crystals of RGa_3 (R = Sc or Lu), formed with superconducting Ga with $T_c = 1.09$ K (Ref. 1) and either nonsuperconducting Sc or superconducting Lu whose critical temperature is $T_c = 0.1$ K.[1]

Past studies focused on the synthesis of polycrystalline samples of RGa_3, with reports on single crystals limited to de Haas van Alphen measurements.[6] Pluzhnikov *et al.*[6] characterized the geometry of the Fermi surface of three related intermetallic compounds, RGa_3 (R = Sc, Lu) and $LuIn_3$. Together with findings from band structure calculations[7] on the same systems, these reports suggested great similarities between the electronic properties of $ScGa_3$ and $LuGa_3$. Superconductivity below 2.3 K in $LuGa_3$ have already been mentioned,[8] but measurements of thermodynamic and transport properties of both $ScGa_3$ and $LuGa_3$ have so far been limited to $T > 4.2$ K.[9,10] The similarities in the electronic structures of $ScGa_3$ and $LuGa_3$ suggest that, if the superconductivity in the latter compound is confirmed, the former is likely to also display a superconducting ground state. In the current paper we show evidence that indeed both RGa_3 (R = Sc and Lu) are superconducting. The low critical temperatures T_c around 2.2 K and small critical fields $H_c < 240$ Oe point to type-I superconductivity in both these compounds. Additional supporting evidence for the type-I superconductivity is provided by the field-dependent specific heat and low values of the Ginzburg-Landau (GL) coefficient $\kappa \approx 0.23$ and 0.3 for $ScGa_3$ and $LuGa_3$, respectively.

II. EXPERIMENTAL METHODS

The RGa_3 compounds (R = Sc, Dy-Tm, Lu) crystallize in the cubic $Pm\bar{3}m$ space group, a structure suggested by Matthias[11] to be favorable for superconductivity. Single crystals of $ScGa_3$ and $LuGa_3$ were prepared using a self flux method by combining Sc or Lu (Hefa Rare Earth 99.999%) with Ga (Alfa Aesar 99.9999%). A R:Ga ratio of 1:9 was mixed in an alumina crucible, heated up to 930 °C, and then slowly cooled down to 760 °C, followed by decanting of the residual flux in a centrifuge. Metallic cubic crystals with well-formed facets up to $2 \times 2 \times 2$ mm^3 in size were obtained. The crystals were then wrapped in Ta foil and annealed at 800 °C for a week. Temperature- and field-dependent magnetization measurements with the magnetic field H parallel to the crystallographic axis $H||a$ were performed in a Quantum Design (QD) Magnetic Property Measurement System, while specific heat data were collected in a QD Physical Property Measurement System (PPMS) using an adiabatic relaxation method. Alternating current resistivity measurements from 0.4 K to 300 K were carried out using the standard four-probe method in the QD PPMS, with the current along the a axis $i = 0.5$ mA and $f = 17.77$ Hz.

Powder x-ray diffraction data, shown in Fig. 1 for $ScGa_3$, were collected for both compounds in a Rigaku D/Max diffractometer using CuKα radiation. The patterns for $ScGa_3$ and $LuGa_3$ were refined with the cubic space group $Pm\bar{3}m$, with lattice parameters $a = 4.09$ Å and $a = 4.19$ Å, respectively. A picture of a $ScGa_3$ crystal is also shown in the inset in Fig. 1. Traces of residual Ga flux are apparent in the powder pattern and are marked with asterisks in Fig. 1. Additional single-crystal x-ray diffraction measurements confirmed the crystal structure, stoichiometry, and purity of the $ScGa_3$ crystals.

III. RESULTS AND DISCUSSION

As-measured susceptibility data $\chi = M/H$ for RGa_3 in various applied magnetic fields H was scaled by 4π and corrected for demagnetizing effects $4\pi\chi_{\text{eff}} = 4\pi\chi/(1 - N_d\chi)$ as shown in Fig. 2. The demagnetizing factor, $N_d \approx 1/3$,[12,13] is associated with the cubic geometry of the crystals. As anticipated from their electronic properties,[6] both R = Sc [Fig. 2(a)] and Lu [Fig. 2(b)] compounds display similar superconducting ground states below 2.2–2.3 K. Increasing magnetic field suppresses the transition for $ScGa_3$ [Fig. 2(a)], such that T_c becomes smaller than 1.8 K for $H \approx 80$ Oe. Figure 2(b) illustrates the similarity between the $H = 5$ Oe $M(T)$ data for $ScGa_3$ (squares) and $LuGa_3$ (triangles), for both zero-field-cooled (solid symbols) and field-cooled (open symbols) data. The critical field H_c for each compound can

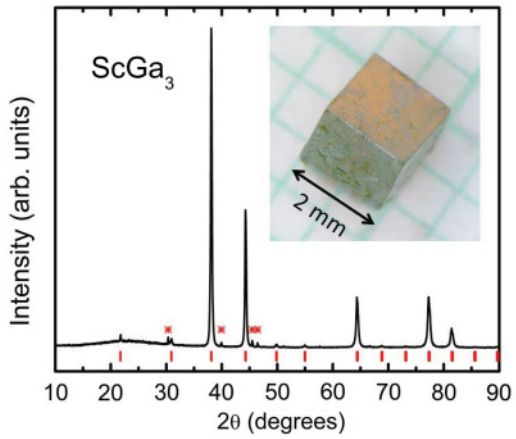

FIG. 1. (Color online) Powder x-ray pattern for $ScGa_3$ (black), with calculated peak positions (vertical red marks) for space group $Pm\bar{3}m$ and lattice parameter $a = 4.0919$ Å. Minute amounts of residual Ga flux are marked by asterisks. Inset: A picture of a single crystal of $ScGa_3$ prepared from a molten solution.

also be estimated from the $M(H)$ data, shown in Fig. 3. Taking the demagnetization effect into consideration, a more accurate estimate of the field H is $H_{\rm eff} = H - N_d M$, where, as before, for a cube and $H||a$, $N_d \approx 1/3$. The resulting $M(H_{\rm eff})$ isotherms are displayed in Fig. 3 (solid symbols, bottom axes) along with as-measured $M(H)$ for $T = 1.8$ K (open symbols, top axes). The critical-field values H_c, corresponding to the entrance to the normal state ($M = 0$), are not changed when demagnetizing effects are taken into account for $H||a$. The critical fields are remarkably low, H_c reaching only about

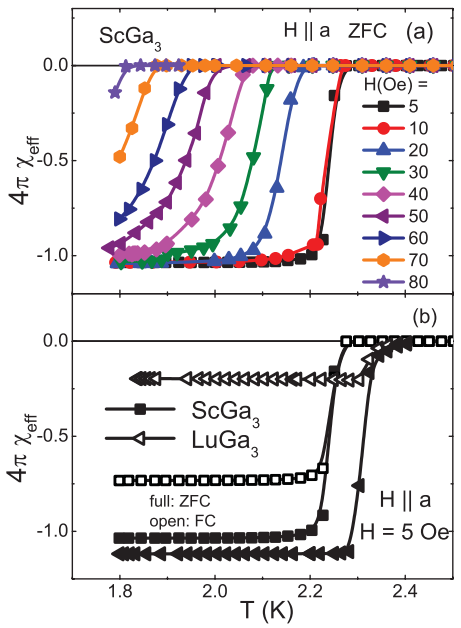

FIG. 2. (Color online) (a) Zero-field-cooled temperature-dependent susceptibility data, scaled by 4π and corrected for demagnetizing effects $4\pi\chi_{\rm eff} = 4\pi\chi/(1 - N_d\chi)$, for $ScGa_3$ in applied magnetic fields up to 80 Oe. (b) $H = 5$ Oe zero-field-cooled (solid symbols) and field-cooled (open symbols) scaled susceptibility $4\pi\chi_{\rm eff}$ data for $ScGa_3$ (squares) and $LuGa_3$ (triangles).

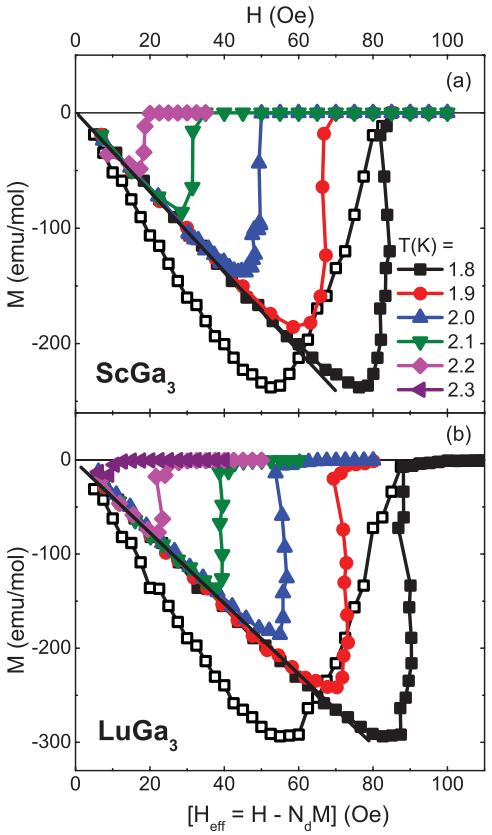

FIG. 3. (Color online) (a) $ScGa_3$ and (b) $LuGa_3$ $M(H_{\rm eff})$ for temperatures between 1.8 K and 2.3 K, where $H_{\rm eff} = H - N_d M$ and N_d is the demagnetizing factor for $H||a$. Open squares: $M(H)$ isotherms for $T = 1.8$ K, where H is the applied (external) magnetic field.

90 Oe at 1.8 K, the lowest temperature available for the magnetization measurements. Moreover, as is shown below, the critical fields for both compounds remain small down to 0.4 K. This observation, along with the small critical temperatures and the shape of the $M(H)$ isotherms, indicates type-I superconductivity in both $ScGa_3$ and $LuGa_3$. While most elemental SCs are type I, this is a rare occurrence in superconducting compounds, making $ScGa_3$ and $LuGa_3$ two of only a few such known systems.[14–18] It is therefore imperious to fully characterize the superconducting state in the RGa_3 SCs. Specific heat and resistivity measurements allow us to extend the findings from magnetization data down to lower temperatures.

Field-dependent specific heat measurements for $ScGa_3$ and $LuGa_3$ were carried out in fields up to 240 Oe, as shown in Fig. 4. As expected, a sharp peak is observed for field values $H < 240$ Oe, from which the critical temperature T_c can be determined as the point halfway between the peak and the normal state specific heat signal. Type-I superconductivity in both compounds is confirmed by the increase of the jump in specific heat between zero and nonzero applied magnetic field H, indicating second- to first order phase transition. T_c for $ScGa_3$ and $LuGa_3$ is suppressed from 2.1 K [open squares, Fig. 4(a)] and 2.0 K [open squares, Fig. 4(b)], respectively, at $H = 0$ to below 0.4 K at $H = 240$ Oe [solid line, Figs. 4(c) and 4(d)]. The normal state electronic specific heat coefficient

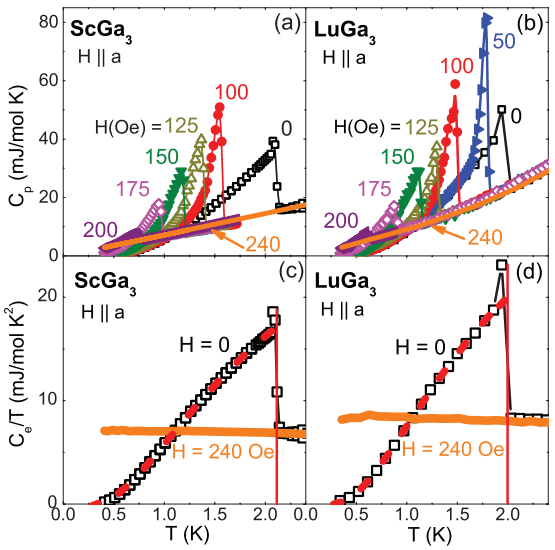

FIG. 4. (Color online) Specific heat data for (a) $ScGa_3$ and (b) $LuGa_3$ in applied magnetic fields up 240 Oe. (c) and (d) Normal ($H = 240$ Oe) and superconducting ($H = 0$) electronic specific heat C_e, scaled by temperature T. The entropy conservation construct gives the ratio $\Delta C_{es}/\gamma_n T_c \approx 1.44$ for both $ScGa_3$ and $LuGa_3$, with the dashed line representing a fit of C_e/T to the expected BCS electronic specific heat.

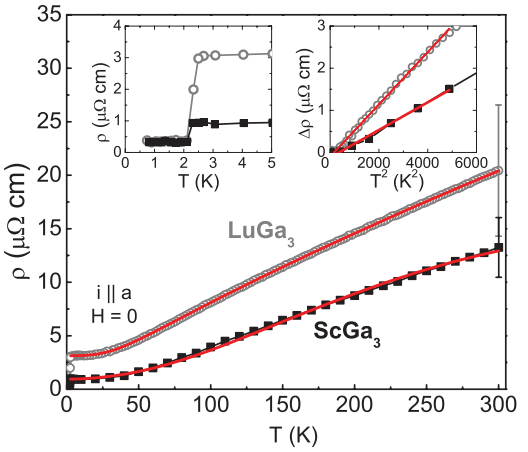

FIG. 5. (Color online) $H = 0$ temperature-dependent resistivity for $ScGa_3$ (solid black symbols) and $LuGa_3$ (open gray symbols), with Bloch-Grüneisen-Mott fits (solid lines) for $n = 2$ ($ScGa_3$) and $n = 3$ ($LuGa_3$). Left inset: Low-temperature $\rho(T)$ around T_c. Right inset: $\Delta\rho = \rho - \rho(0)$ vs T^2, with solid lines representing linear fits up to 80 K for $ScGa_3$ and 70 K for $LuGa_3$.

γ_n and phonon specific heat coefficient β were estimated from the linear fit of the normal state ($H = 240$ Oe) specific heat below 8 K, plotted as C_p/T vs T^2 (not shown). Very similar γ_n values, 7.11 and 8.46 mJ mol^{-1} K^{-2}, were obtained for $ScGa_3$ and $LuGa_3$, respectively. The experimental γ_n values are larger than those estimated ($\gamma_{n,\mathrm{PPPW}} = 2.4$ mJ/mol K^2 for $ScGa_3$ and 1.2 mJ/mol K^2 for $LuGa_3$) from existing band structure calculations based on the Pseudopotential Plane-Wave Approximation (PPPW).[7] However, a more accurate estimate of γ_n results from the Full Potential Linear Augmented Plane-Wave Method (FPLAPW),[19] which gives $\gamma_{n,\mathrm{FPLAPW}} = 7.1$ mJ/mol K^2 for $ScGa_3$, identical with the experimental value of 7.11 mJ/mol K^2. The superconducting electronic specific heat coefficient γ_s can also be determined from γ_n and the residual electronic specific heat coefficient γ_{res}. The latter coefficient, γ_{res}, estimated from C_e/T at $T = 0.4$ K and $H = 0$ [Figs. 4(c) and 4(d)], is much smaller than γ_n for both compounds. This results in $\gamma_s = \gamma_n - \gamma_{\mathrm{res}} \approx \gamma_n$ for both $ScGa_3$ and $LuGa_3$. The entropy-conservation construct shown in Figs. 4(c) and 4(d) for $ScGa_3$ and $LuGa_3$, respectively, yields the same value for the jump in the electronic specific heat C_e at T_c, $\Delta C_e/\gamma_n T_c \approx 1.44$, consistent with BCS-type superconductivity.[20] One more similarity between the two compounds is the minimum excitation energy $\Delta(0)$: from the low-temperature fit of the electronic specific heat $C_e \propto e^{-\Delta/k_B T}$ [dashed lines in Figs. 4(c) and 4(d)], $\Delta(0)$ is estimated to be 0.18 meV for $ScGa_3$ and 0.17 meV for $LuGa_3$. The Debye temperature $\theta_D = (12\pi^4 N_A r k_B/5\beta)^{1/3}$, where $r = 4$ is the number of atoms per formula unit, can be determined using the phonon specific heat coefficient β (Table I), also estimated from the linear fit of C_p/T vs T^2 (not shown). This yields $\theta_D = 660$ K for $ScGa_3$ and 232 K for $LuGa_3$. Moreover, the electron-phonon coupling constant $\lambda_{\text{el-ph}}$, can be determined using McMillan's theory:[21]

$$\lambda_{\text{el-ph}} = \frac{1.04 + \mu^* \ln(\theta_D/1.45T_c)}{(1 - 0.62\mu^*)\ln(\theta_D/1.45T_c) - 1.04},$$

where μ^* represents the repulsive screened Coulomb potential and is usually between 0.1 and 0.15. Setting $\mu^* = 0.13$, $\lambda_{\text{el-ph}} = 0.45$ and 0.55 for $ScGa_3$ and $LuGa_3$, respectively, which implies that both compounds are weakly coupled SCs.

From the specific heat data for both the superconducting ($H = 0$) and the normal ($H = 240$ Oe) states, an estimate of the thermodynamic critical field H_c can be obtained using the free energy relation.[22] The thermodynamic critical field values $H_c = 209 \pm 10$ Oe for $ScGa_3$ and $H_c = 226 \pm 10$ Oe for $LuGa_3$ are consistent with what has been observed in magnetization and specific heat data. The field- and temperature-dependent data can be summarized in the H-T phase diagram shown in Fig. 6 and discussed below.

Previously reported resistivity measurements[9,10] on $LuGa_3$ were limited to temperatures above 4.2 K, while similar data had not been presented for $ScGa_3$. Figure 5 displays the $H = 0$ resistivity data for $ScGa_3$ and $LuGa_3$ (solid and open symbols,

TABLE I. Summary of parameters describing $ScGa_3$ and $LuGa_3$ properties.

	T_c (K)	H_c (Oe)	γ_n (mJ mol^{-1} K^{-2})	β (mJ mol^{-1} K^{-4})	A ($\mu\Omega$cm K^{-2})	RRR	$\frac{\Delta C_e(T_c)}{\gamma_n T_c}$	$\lambda_{\text{el-ph}}$	m^* (m_0)	λ (nm)	ξ (μm)	κ
$ScGa_3$	2.1 ± 0.2	209 ± 10	7.03 ± 0.08	0.027	3.4×10^{-4}	14.0	1.44	0.45	3.03	59	0.26	0.23
$LuGa_3$	2.2 ± 0.25	226 ± 10	8.52 ± 0.06	0.621	6.1×10^{-4}	6.5	1.44	0.55	3.49	63	0.21	0.30

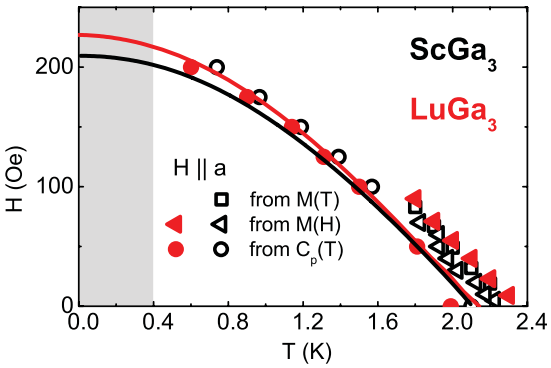

FIG. 6. (Color online) H-T phase diagram for $ScGa_3$ (open black symbols) and $LuGa_3$ (solid red symbols). The values of the critical field H_c are determined from $M(T)$ data (squares), $M(H)$ data (triangles), and $C_p(T)$ data (circles).

respectively). The superconducting transition (left inset) is around 2.2–2.3 K for both compounds. The apparently finite resistivity in the superconducting state is likely an artifact of the measurement: the overall resistivity values are very small for both compounds; below T_c, the contact resistance, albeit small, might alter the measured voltage, which is very close to the instrument resolution. Above the transition and below 80 K for $ScGa_3$ or 70 K for $LuGa_3$, $\rho(T)$ exhibits Fermi liquid behavior, as illustrated by the $\Delta\rho \propto AT^2$ plot, with $A = 3.4 \times 10^{-4}$ and 6.1×10^{-4} $\mu\Omega$cm K^{-2}, respectively (right inset, Fig. 5). At higher temperatures a slight curvature of the resistivity is apparent. Fits to the Bloch-Grüneisen-Mott (BGM) relation[23] (solid lines, Fig. 5)

$$\rho = \rho_0 + A\left(\frac{T}{\theta_D}\right)^n \int_0^{\theta_D/T} \frac{x^n dx}{(e^x - 1)(1 - e^{-x})} - kT^3,$$

with $n = 2$ for $ScGa_3$ and $n = 3$ for $LuGa_3$, describe the data well up to room temperature, even higher than $\theta_D/4$. This points to significant s-d band scattering, while the different exponents n suggest underlying differences in the electron-phonon scattering in the two compounds. The fits shown in Fig. 5 were performed using the θ_D values determined from specific heat; the other BGM parameters were determined to be $A = 38.5$ and 28.6 $\mu\Omega$cm and $k = 1.3 \times 10^{-7}$ and 0.3×10^{-7} $\mu\Omega$cm/K^3, for $ScGa_3$ and $LuGa_3$, respectively. If the parameter θ is also released for the BGM fits, equally good fits for $n = 2$ and $n = 3$ are achieved for $ScGa_3$, for θ_R values between 320 K and 460 K, significantly smaller than the Debye temperature $\theta_D = 660$ K. For $LuGa_3$, the parameters remain nearly unchanged, with the best fit for $n = 3$ and $\theta_R = 230$ K virtually identical to $\theta_D = 232$ K.

Based on the Sommerfield coefficient extracted from the specific heat data, it is possible to estimate the London penetration depth $\lambda_L(0)$, the coherence length $\xi(0)$, and the GL parameter $\kappa(0) = \lambda_L(0)/\xi(0)$. Since both $ScGa_3$ and $LuGa_3$ have one formula unit per unit cell, the conduction electron density n, due to three electrons contributed by Sc and Lu, can be estimated as $n = 3/V$, where V is the volume of the unit cell. It results that $n = 4.39 \times 10^{-2}$ Å^{-3} and $n = 4.08 \times 10^{-2}$ Å^{-3} for $ScGa_3$ and $LuGa_3$, respectively. If a spherical Fermi surface is assumed for both compounds, the Fermi wave vector k_F can be roughly calculated as $k_F = (3n\pi^2)^{1/3} = 1.09$ Å^{-1} for $ScGa_3$ and 1.07 Å^{-1} for $LuGa_3$. The effective electron mass can then be determined as $m^* = \hbar^2 k_F^2 \gamma_n / \pi^2 n k_B^2 = 3.03 m_0$ and $3.49 m_0$ for $ScGa_3$ and $LuGa_3$, respectively, where m_0 is the free electron mass. The London penetration depth is given as $\lambda_L(0) = (m^*/\mu_0 n e^2)^{1/2} = 59$ nm for $ScGa_3$ and 63 nm for $LuGa_3$. The coherence length is then determined as $\xi = 0.18\hbar k_F / k_B T_c m^* = 0.26$ μm and 0.21 μm for $ScGa_3$ and $LuGa_3$, respectively. The GL parameter $\kappa(0) = \lambda_L(0)/\xi(0)$ is thus 0.23 for $ScGa_3$ and 0.30 for $LuGa_3$. This indicates that both compounds are type-I SCs, since $\kappa < 1/\sqrt{2}$. By comparison, MgB_2 is an example of a type-II SC and its $\kappa(0)$ is close to 26,[24] while $\kappa(0)$ for $LaRhSi_3$, a reported type-I superconducting compound, is close to 0.25.[14]

IV. CONCLUSIONS

In summary, type-I superconductivity in $ScGa_3$ and $LuGa_3$ is reported, with the parameters characteristic of the superconducting state shown in Table I. The shape of the $M(H)$ isotherms (Fig. 3), field-induced second- to first-order phase transition in specific heat (Fig. 4), and low T_c, H_c, and κ values (Table I) suggest that $ScGa_3$ and $LuGa_3$ are both type-I superconducting compounds. This is reflected also in the H-T phase diagram (Fig. 6), where the symbols represent experimental points from $M(T)$ (squares), $M(H)$ (triangles), and C_P (circles). These data are in good agreement with the thermodynamic critical field H_c temperature dependence (solid lines). As suggested by the electronic properties,[6] the superconducting parameters for the two compounds are very similar, as are their H-T phase diagrams. A careful analysis of the crystal structure on one hand and the thermodynamic and transport properties of the type-I superconducting compounds on the other hand may offer valuable insights into the rare occurrence of type-I superconductivity in binary or ternary systems. The relatively small electron-phonon coupling parameter $\lambda_{\text{el-ph}}$ indicates that both compounds are weakly coupled BCS SCs.

ACKNOWLEDGMENTS

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