Type-I superconductivity in ScGa3 and LuGa3 single crystals

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We present evidence of type-I superconductivity in single crystals of ScGa3 and LuGa3, from magnetization, specific heat, and resistivity measurements: low critical temperatures \( T_c \) = 2.6–2.2 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 ScGa3 and LuGa3, respectively, are all traits of a type-I superconducting ground state. These observations render ScGa3 and LuGa3 two of only several type-I superconducting compounds, with most other superconductors being type II (compounds and alloys) or type I (elemental metals and metalloids).

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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 \( T_c \). It has been noted\(^1\) that intermetallic compounds often have \( T_c \) values higher than those of the constituent elements, as is the case in Nb2Sn, V3Si, ZrB2, and NbB2.\(^5\) In this work, we present thermodynamic and transport measurements on single crystals of \( R \)Ga3 (\( R = \) 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.\(^4\)

Past studies focused on the synthesis of polycrystalline samples of \( R \)Ga3, 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, \( R \)Ga3 (\( R = \) Sc, Lu) and LuGa3. Together with findings from band structure calculations\(^1\) on the same systems, these reports suggested great similarities between the electronic properties of ScGa3 and LuGa3. Superconductivity below 2.3 K in LuGa3 have already been mentioned,\(^8\) but measurements of thermodynamic and transport properties of both ScGa3 and LuGa3 have so far been limited to \( T > 4.2 \) K.\(^9,10\) The similarities in the electronic structures of ScGa3 and LuGa3 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 ScGa3 (\( R = \) 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 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 ScGa3 and LuGa3, respectively.

II. EXPERIMENTAL METHODS
The \( R \)Ga3 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 ScGa3 and LuGa3 were prepared using a self flux method by combining Sc or Lu (Hefa Rare Earth 99.999\%) with Ga (Alfa Aesar 99.999\%). 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 ScGa3, were collected for both compounds in a Rigaku D/Max diffractometer using CuK\( \alpha \) radiation. The patterns for ScGa3 and LuGa3 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 ScGa3 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 ScGa3 crystals.

III. RESULTS AND DISCUSSION
As-measured susceptibility data \( \chi = M/H \) for \( R \)Ga3 in various applied magnetic fields \( H \) was scaled by 4\( \pi \) 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, \( N_d \approx 1/3 \), 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 ScGa3 [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 ScGa3 (squares) and LuGa3 (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 \(a = 4.0919\ \text{Å}\). 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 \(H_{\text{eff}} = H - N_d M\), where, as before, for a cube and \(H \parallel a\), \(N_d \approx 1/3\). The resulting \(M(H_{\text{eff}})\) isotherms are displayed in Fig. 3 (solid symbols, bottom axes) along with as-measured \(M(H)\) for \(T = 1.8\ \text{K}\) (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 \(H \parallel a\). The critical fields are remarkably low, \(H_c\) reaching only about 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 \(R\)Ga$_3$ 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 \(H < 240\ \text{Oe}\), 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 \(H = 240\ \text{Oe}\) [solid line, Figs. 4(c) and 4(d)]. The normal state electronic specific heat coefficient

FIG. 2. (Color online) (a) Zero-field-cooled temperature-dependent susceptibility data, scaled by \(4\pi\) and corrected for demagnetizing effects \(4\pi\chi_{\text{eff}} = 4\pi\chi/(1 - N_d\chi)\), for ScGa$_3$ in applied magnetic fields up to 80 Oe. (b) \(H = 5\ \text{Oe}\) zero-field-cooled (solid symbols) and field-cooled (open symbols) scaled susceptibility \(4\pi\chi_{\text{eff}}\) data for ScGa$_3$ (squares) and LuGa$_3$ (triangles).

FIG. 3. (Color online) (a) ScGa$_3$ and (b) LuGa$_3$ \(M(H_{\text{eff}})\) for temperatures between 1.8 K and 2.3 K, where \(H_{\text{eff}} = H - N_d M\) and \(N_d\) is the demagnetizing factor for \(H \parallel a\). Open squares: \(M(H)\) isotherms for \(T = 1.8\ \text{K}\), where \(H\) is the applied (external) magnetic field.
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γₙ 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 T² (not shown). Very similar γₙ values, 7.11 and 8.46 mJ mol⁻¹ K⁻², were obtained for ScGa₃ and LuGa₃, respectively. The experimental γₙ values are larger than those estimated (γₙ,PPPW = 2.4 mJ mol⁻¹ K² for ScGa₃ and 1.2 mJ mol⁻¹ K² for LuGa₃) from existing band structure calculations based on the Pseudopotential Plane-Wave Approximation (PPPW). However, a more accurate estimate of γₙ results from the Full Potential Linear Augmented Plane-Wave Method (FPLAPW), which gives γₙ,FPLAPW = 7.1 mJ mol⁻¹ K² for ScGa₃, identical with the experimental value of 7.11 mJ mol⁻¹ K². The superconducting electronic specific heat coefficient γₛ can also be determined from γₙ and the residual electronic specific heat coefficient γ_res. The latter coefficient, γ_res, estimated from C/γₙ in T = 0.4 K and H = 0 (Figs. 4(c) and 4(d)), is much smaller than γₙ for both compounds. This results in γₛ = γₙ - γ_res ≈ γₙ for both ScGa₃ and LuGa₃. The entropy-conservation construct shown in Figs. 4(c) and 4(d) for ScGa₃ and LuGa₃, respectively, yields the same value for the jump in the electronic specific heat C_e at T_c, ΔC_e/γₙT_c ≈ 1.44, consistent with BCS-type superconductivity.

One more similarity between the two compounds is the minimum excitation energy Δ(0) from the low-temperature fit of the electronic specific heat C_e ∝ e⁻Δ/κT [dashed lines in Figs. 4(c) and 4(d)], Δ(0) is estimated to be 0.18 meV for ScGa₃ and 0.17 meV for LuGa₃. The Debye temperature θ_D = (12π⁴NArkB/5β)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 T² (not shown). This yields θ_D = 660 K for ScGa₃ and 232 K for LuGa₃. Moreover, the electron-phonon coupling constant λ_el-ph, can be determined using McMillan’s theory:

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

where μ* represents the repulsive screened Coulomb potential and is usually between 0.1 and 0.15. Setting μ* = 0.13, λ_el-ph = 0.45 and 0.55 for ScGa₃ and LuGa₃, 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. The thermodynamic critical field values H_c = 209 ± 10 Oe for ScGa₃ and H_c = 226 ± 10 Oe for LuGa₃ 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 on LuGa₃ were limited to temperatures above 4.2 K, while similar data had not been presented for ScGa₃. Figure 5 displays the H = 0 resistivity data for ScGa₃ and LuGa₃ (solid and open symbols, with Bloch-Grüneisen-Mott fits (solid lines) for n = 2 (ScGa₃) and n = 3 (LuGa₃). Left inset: Low-temperature ρ(T) around T_c. Right inset: Δρ = ρ - ρ(0) vs T², with solid lines representing linear fits up to 80 K for ScGa₃ and 70 K for LuGa₃.

![FIG. 5. (Color online) H = 0 temperature-dependent resistivity for ScGa₃ (solid black symbols) and LuGa₃ (open gray symbols), with Bloch-Grüneisen-Mott fits (solid lines) for n = 2 (ScGa₃) and n = 3 (LuGa₃). Left inset: Low-temperature ρ(T) around T_c. Right inset: Δρ = ρ - ρ(0) vs T², with solid lines representing linear fits up to 80 K for ScGa₃ and 70 K for LuGa₃.](image)

TABLE I. Summary of parameters describing ScGa₃ and LuGa₃ properties.

<table>
<thead>
<tr>
<th></th>
<th>T_c (K)</th>
<th>H_c (Oe)</th>
<th>γₙ</th>
<th>β</th>
<th>A (µΩcm K⁻²)</th>
<th>RRR</th>
<th>ΔC_e(T_c)</th>
<th>λ_el-ph</th>
<th>m* (ma)</th>
<th>λ (nn)</th>
<th>ξ (μm)</th>
<th>κ</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScGa₃</td>
<td>2.1 ± 0.2</td>
<td>209 ± 10</td>
<td>7.03 ± 0.08</td>
<td>0.027</td>
<td>3.4 × 10⁻⁴</td>
<td>14.0</td>
<td>1.44</td>
<td>0.45</td>
<td>3.03</td>
<td>59</td>
<td>0.26</td>
<td>0.23</td>
</tr>
<tr>
<td>LuGa₃</td>
<td>2.2 ± 0.25</td>
<td>226 ± 10</td>
<td>8.52 ± 0.06</td>
<td>0.621</td>
<td>6.1 × 10⁻⁴</td>
<td>6.5</td>
<td>1.44</td>
<td>0.55</td>
<td>3.49</td>
<td>63</td>
<td>0.21</td>
<td>0.30</td>
</tr>
</tbody>
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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 below 80 K for ScGa3 or 70 K for LuGa3, $\rho_{\text{c}}(T)$ exhibits Fermi liquid behavior, as illustrated by the $\Delta \rho \propto AT^2$ plot, with $A = 3.4 \times 10^{-4}$ and $6.1 \times 10^{-4} \mu\Omega\text{cm} K^{-2}$, respectively (right inset, Fig. 5). At higher temperatures a slight curvature of the resistivity is apparent. Fits to the Bloch-Grüneisen-Mott (BGM) relation (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 ScGa3 and $n = 3$ for LuGa3, 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 $\theta_D$ values determined from specific heat; the other BGM parameters were determined to be $A = 38.5$ and $28.6 \mu\Omega\text{cm}$ and $k = 1.3 \times 10^{-2}$ and $0.3 \times 10^{-1} \mu\Omega\text{cm}/K^3$, for ScGa3 and LuGa3, respectively. If the parameter $\theta_D$ is also released for the BGM fits, equally good fits for $n = 2$ and $n = 3$ are achieved for ScGa3 and LuGa3, respectively. The $\theta_D$ values between 320 K and 460 K, significantly smaller than the Debye temperature $\theta_D = 660$ K. For LuGa3, the $\theta_D$ values remain nearly unchanged, with the best fit for $n = 3$ and $\theta_D = 230$ K virtually identical to $\theta_D = 232$ K.

Based on the Sommerfeld 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 ScGa3 and LuGa3 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 ScGa3 and LuGa3, respectively. If a spherical Fermi surface is assumed for both compounds, the Fermi wave vector $k_F$ can be roughly calculated as $k_F^* = \sqrt{2} k_F^* \gamma_0 / n^2 k_F^0 = 3.03 m_0$ and $3.49 m_0$ for ScGa3 and LuGa3, respectively, where $m_0$ is the free electron mass. The London penetration depth is given as $\lambda_L(0) = (m^* / \mu_0 n^3 e^2)^{1/2} = 59$ nm for ScGa3 and 63 nm for LuGa3. The coherence length is then determined as $\xi = 0.18 h k_F / k_B T_c m^* = 0.26 \mu$m and $0.21 \mu$m for ScGa3 and LuGa3, respectively. The GL parameter $\kappa(0) = \lambda_L(0)/\xi(0)$ is thus 0.23 for ScGa3 and 0.30 for LuGa3. This indicates that both compounds are type-I SCs, since $\kappa < 1/\sqrt{2}$. By comparison, MgB2 is an example of a type-II SC and its $\kappa(0)$ is close to 26,24 while $\kappa(0)$ for LaRhSi3, a reported type-I superconducting compound, is close to 0.25.14

**IV. CONCLUSIONS**

In summary, type-I superconductivity in ScGa3 and LuGa3 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 $\kappa$ values (Table I) suggest that ScGa3 and LuGa3 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, 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 $\lambda_{e-ph}$ indicates that both compounds are weakly coupled BCS SCs.

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M. Tinkham, Introduction to Superconductivity, 2nd ed. (Dover, New York, 1996).
