Superconductivity in $LuGe_2$

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We report the discovery of a superconductor $LuGe_2$. Magnetic and electrical measurements showed that the transition temperature $T_c = 2.6 \pm 0.1$ K. Powder x-ray diffraction patterns indicate that this compound has the orthorhombic $ZrSi_2$-type structure with space group C_{mcm}. A refinement of the lattice parameters of the unit cell, determing by the method of least squares using the thirteen intense reflections for $2\theta < 60°$, showed that $a = 0.3969(9)$, $b = 1.5553(3)$, and $c = 0.3839(9)$ nm. In addition, no superconducting transition above 1.8 K was observed for the nonstrochiometric compound $LuGe_{1.5}$ with AlB_2-type structure.

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Three superconducting rate-earth digermanides, namely, $ScGe_2$ ($T_c = 1.30-1.31$ K), YGe_2 ($T_c = 3.8$ K), and $LaGe_2$ ($T_c = 1.49$ K) were discovered by Matthias *et al.* 46 year ago.[1] Recently, two superconducting germanides with AlB_2-type structure Y_2PdGe_3 (Refs. 2–4) and $Y(Pt_{0.5}Ge_{1.5})$ (Ref. 5), have been reported. It looks that previous literature presents far less information in the structure or superconducting properties for the germanides than for the silicides or borides. The AlB_2-type structure has been noticed to be a possible structure for high T_c superconductor since the gaining knowledge of superconductivity at 39 K in MgB_2.[6] Earlier x-ray diffraction data showed that the nonstoichiometric compounds RGe_{2-x} (R = Y, Nd, Sm, Gd-Lu) exhibited AlB_2-type structure and displayed additional diffracted intensities suggesting ordering of the Ge vacancies.[7,8] Inspite of the fact that nonsuperconductivity observed in these nonstoichiometric rate earth germanides with AlB_2-type structure, we have found that the lutetium digermanide $LuGe_2$, which crystallizes in an orthorhombic $ZrSi_2$-type structure with space group C_{mcm},[9,10] displays a superconducting phase transition at 2.6 ± 0.1 K as determined from direct current (dc) susceptibility and electrical resistivity measurements.

Polycrystalline samples investigated for this work were synthesized by arc melting together appropriate amounts of the components on a water-cooled Cu hearth in 1 atm of high-purity argon gas in which a Zr button used as an oxygen getter had been previously arc melted. The rare-earth element (Lu) of 99.9% (3N) purity was obtained from the Materials Preparation Center of the Ames Laboratory. The 5 N purity Ge were purchased from Alfa Aesar, a Johnson Matthey company. Due to sufficiently low vapor pressures of these elements at the melting temperature of the binary compound, evaporation losses can be neglected. The as arc-melted sample was sealed under argon in a quartz tube, and annealed for 2 days at 1000 °C. This heat treatment was followed by a water quench to room temperature. A microcomputer controlled MXP3 diffractometer equipped with copper target and graphite monochrometor for Cu K_α radiation ($\lambda = 1.54056$ Å) was used to get the powder x-ray diffraction patterns at a scan rate of 0.4°/min. The observed powder x-ray diffraction patterns at room temperature for the sample $LuGe_2$ is shown in Fig. 1. The sharp and indexed peak of the observed pattern confirm that the compound crystallizes in an orthorhombic structure with space group C_{mcm}. However, there is an additional weak line (marked by × in Fig. 1) at $2\theta = 27.42°$, which is due to the impurity phase of Ge(111) line. At the present stage, it cannot be excluded that the orthorhombic phase consists of a small amount of nonstoichiometric germanium composition because the exact germaium content has not been determined experimentally in this study. A refinement of the lattice parameters of the unit cell was made from the powder x-ray diffraction patterns by the method of least squares using the thirteen most intense reflections for $2\theta < 60°$. The lattice parameters $a = 0.3969(9)$, $b = 1.5553(3)$, and $c = 0.3839(9)$nm for $LuGe_2$ were then obtained. In this refinement to determine lattice parameters, only the positions of the x-ray lines were required. A camparison of the calculated line intensities with those determined experimentally showed reasonable agreement, especially considering the nature of powder x-ray data for a quantitative determination of line intensities. In this comparison, we used standard atomic positional parameters for the atoms in the unit cell. Specifically, the atoms were all placed in the 4*c* position of the space group $C_{mcm}(D_{2h}^{17})$ with fractional coordinates: Ge(1) (0, 0.435, 0.25), Ge(2) (0, 0.750, 0.25), and Lu (0, 0.103, 0.25). The agreement of intensities indicates that no significant antisite disorder or vacancies are present in our sample.

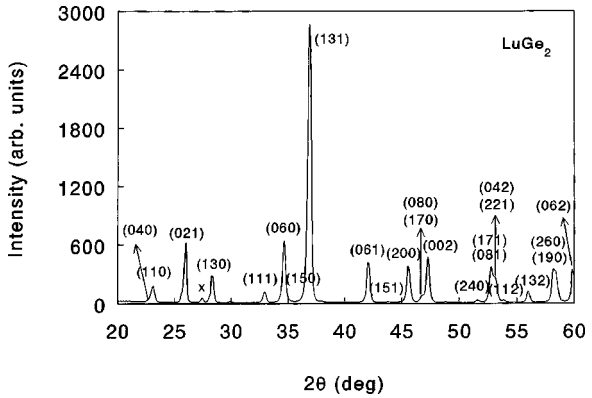

FIG. 1. Room temperature powder x-ray-diffraction patterns of $LuGe_2$ using Cu K_α radiation. The one less intense peak line with × mark belongs to the impurity phase of Ge(111) line.

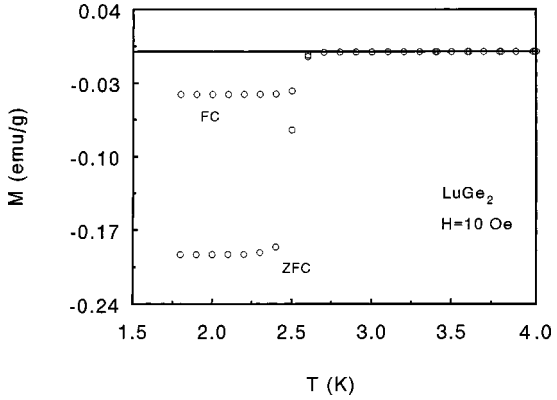

FIG. 2. Temperature dependence of the ZFC and magnetization data for the compound $LuGe_2$ measured in a field of $H=10$ Oe between 1.8 and 4.0 K.

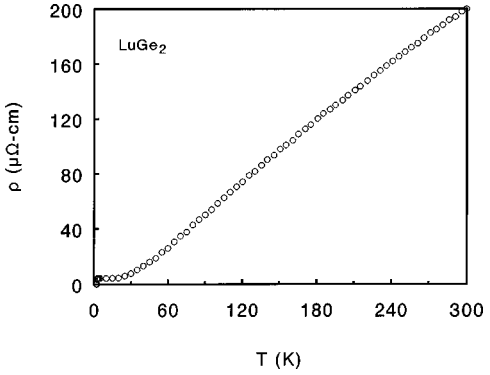

FIG. 3. Electrical resistivity vs temperature between 1.8 for 300 K for $LuGe_2$.

Figure 2 displays the temperature dependence of magnetization measured on a bulk sample of about 0.15 g mass in a Quatum Design superconducting quatum interference device magnetometer. The measurements were carried out in a magnetic field of 10 Oe on heating after zero-field cooling (ZEC) and then on cooling in field (FC). The ZFC curve for the sample $LuGe_2$ show sharp transition from paramagnetic state to superconducting state around 2.6 K and reach saturation at the lower temperature. It is seen that the 10–90% values of the superconductig transition signal occur at the temperatures 2.43 and 2.58 K and $T_{c,\mathrm{mid}}$ is 2.49 K. The quite narrow transition width (0.15 K) is a manifestation of purity of the superconducting phase. In addition, this sample also shows large shielding signals. Excluding any correction for demagnetization effects or size effects to our sample, we calculate a diamagnetic effect (from ZFC data) of 217% of $-1/4\pi$ (the ideal value of χ_{dc} for a long cylinder). This phenomenon can be explained in terms of the geometrical demagnetization factor $n=0.56$ because of the irregular shaped sample. The Meissner flux expulsion (from FC data) is about 21% of the diamagnetic flux expulsion. This reduced Meissner flux expulsion is a characteristic of pinning effect in the compound. The large superconducting volume fraction estimated at 1.8 K is presumably able to constitute bulk superconductivity.

dc electrical resistivity measurements were made between 1.8 and 300 K using a standard four-probe technique in a system fully automated for temperature stability and data acquisition.[11] The sample was small rectangular parallelpiped of approximate dimensions $1\times1\times5$ mm^3. Fine platinum wires ($\sim$2 ml diameter) were spot welded to the rectangular-shaped sample, and served as the voltage and current leads. Data were taken with the current (10 mA) applied in both directions to eliminate possible thermal effects. All data presented are for the warming curve. For each point of the resistivity measurements, temperature control was achieved to an accuracy of 0.1% by using a built-in temperature controller provided by the sample property measurement system.[11] Figure 3 presents the complete resistivity data between 1.8 and 300 K for the polycrystalline sample $LuGe_2$. It is seen that the residual resistivity and residual resistivity ratio values for superconducting $LuGe_2$ are 4.2 $\mu\Omega$ cm and 47.6, respectively. The large residual resistivity ratio indicates that the crystallinity of the sample $LuGe_2$ is quite good. As shown in Fig. 4, which is an enlargement pattern around the superconducting transition point, the onset temperature is 2.7 K and the zero resistivity temperature is attained below 2.6 K. The onset temperature determined by electrical measurements is found to be slightly higher than the transition point value obtained by dc magnetization measurements. This phenomenon is probably due to the surface superconductivity[12,13] of this compound, or due to the different effective time scales involved in magnetic and electric measurements. The critical temperature T_c defined as the midpoint transition is 2.65 K.

As a concluding remark, we found that the binary lutetium digermanide $LuGe_2$ exhibits superconductivity with $T_c \sim 2.6\pm0.1$ K, as characterized by the magnetic and resistivity data. Irrespective of the high-T_c in MgB_2 with AlB_2-type structure, no superconductivity has been reported for the nonstoichiometric rare earth germanides $YGe_{1.5}$ (Ref. 14) and $LaGe_{1.5}$ (Ref. 15) with AlB_2-type structure. In fact, we

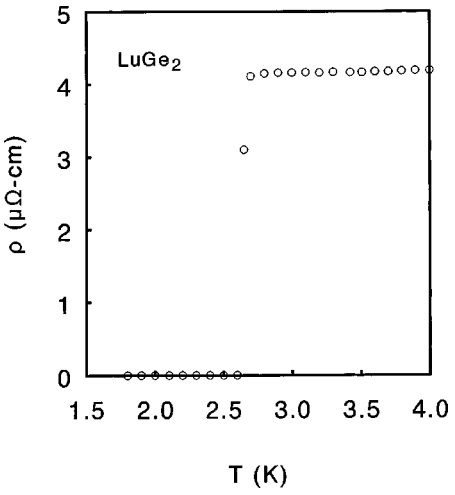

FIG. 4. Electrical resistivity vs temperature between 1.8 and 4.0 K for $LuGe_2$.

also found that the nonstoichiometric yttrium silicide $YSi_{1.7}$ could form single-phased AlB_2-type structure but no superconducting signal was detected above 1.8 K.[16] Among the rare-earth digermanides having the same electron concentration, only those with the $ThSi_2$-type structure (YGe_2) and ($LuGe_2$) (Ref. 14 and 17) and the $ZrSi_2$-type structure ($ScGe_2$) and $LuGe_2$ (Refs. 9, 10, and 14) have been found to be superconducting.

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