Exceedingly small moment itinerant ferromagnetism of single crystalline La$_5$Co$_2$Ge$_3$

S. M. Saunders,$^{1,2}$ L. Xiang$^1$, R. Khasanov,$^3$ T. Kong$^{1,2,*}$ Q. Lin,$^{1,4}$ S. L. Bud’ko,$^{1,2}$ and P. C. Canfield$^{1,2}$

$^1$Ames Laboratory, U.S. DOE, Iowa State University, Ames, Iowa 50011, USA
$^2$Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA
$^3$Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institute, 5232 Villigen, Switzerland
$^4$Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA

DOI: 10.1103/PhysRevB.101.214405

(Received 25 February 2020; accepted 13 May 2020; published 1 June 2020)

Single crystals of monoclinic La$_5$Co$_2$Ge$_3$ were grown using a self-flux method and were characterized by room-temperature powder x-ray diffraction, anisotropic temperature- and field-dependent magnetization, temperature-dependent resistivity, specific heat, and muon spin rotation. La$_5$Co$_2$Ge$_3$ has a Curie temperature ($T_C$) of 3.8 K and clear signatures of ferromagnetism in magnetization and $\mu$SR data, as well as a clear loss of spin disorder scattering in resistivity data and a sharp specific heat anomaly. The magnetism associated with La$_5$Co$_2$Ge$_3$ is itinerant with a change in the entropy at $T_C$ of $\pm 0.05R\ln 2$ per mol Co and has a low-field saturated moment of $\sim 0.1 \mu_B$/Co, making it a rare, itinerant, small moment, low-$T_C$ compound.

Magnetism in metallic compounds has typically been described in a local moment or itinerant moment picture. The local moment description has been studied across many systems, due, in part, to the convenience of rare-earth elements containing partially filled 4f shells which provide well defined, local magnetic moments [1]. There are fewer examples of itinerant magnetism, especially ferromagnetic systems with very low Curie temperature $T_C$ and saturated magnetic moment $\mu_{sat}$. For example, Sc$_2$In [2], ZrZn$_2$ [3], MnSi [4], LuFe$_2$Ge$_2$ [5,6], and TiAu [7] have been suggested to be itinerant with low transition temperatures: $T_C = 6$ and 35 K for the ferromagnetic Sc$_2$In and ZrZn$_2$, respectively, and $T_N = 29$, 9, and 36 K for the antiferromagnetic MnSi, LuFe$_2$Ge$_2$, and TiAu, respectively.

In this manuscript, we report the discovery and basic properties of the itinerant ferromagnet (IFM) La$_5$Co$_2$Ge$_3$. La$_5$Co$_2$Ge$_3$ is composed of 50% non-moment-bearing La, 30% Ge, and only 20% Co; transport and thermodynamic measurements exhibit a Curie temperature of $T_C = (3.8 \pm 0.1)K$, which is one of the lowest reported transition temperatures for an ordered, stoichiometric IFM. Temperature- and field-dependent magnetization measurements reveal $\mu_{eff} = (1.10 \pm 0.05)\mu_B$/Co, whereas the low-field $\mu_{sat} = 0.1\mu_B$/Co leading to a Rhodes-Wohlfarth ratio [8] of 4.9. In addition, specific heat data show a greatly reduced loss of entropy, $0.05R\ln 2$ per mol Co, associated with the transition. Muon spin rotation ($\mu$SR) measurements indicate static moments and internal fields consistent with a greatly reduced ordered moment magnitude when compared to full-moment Co.

Single crystals of La$_5$Co$_2$Ge$_3$ were grown using a self-flux solution growth method [9–11]. The initial composition of the three elements was La:Co:Ge = 45:45:10. The starting elements (Co (99.9%), Ge (Alfa Aesar 99.9% +%), and La (Ames Lab 99.9%)) were combined in a three-cap tantalum crucible [9,10] and sealed in a fused silica ampoule under a partial argon atmosphere. The ampoule was then heated to 1180 °C, held at 1180 °C for 4 hours and slowly cooled to 800 °C over 40 hours at which point the remaining solution was decanted with the assistance of a centrifuge. The crystals of La$_5$Co$_2$Ge$_3$ grew in thin plates as well as long blades, as shown in Fig. 1. The crystals are not air sensitive.

La$_5$Co$_2$Ge$_3$ is isoostructural to Pr$_5$Co$_2$Ge$_3$ [11]; the crystal structure was established at room temperature and ambient pressure using a Rigaku Miniflex powder x-ray diffractometer (Cu $K_{\alpha}$ radiation). Samples were prepared by grinding a single crystal into powder, which was then mounted and measured on a single crystal Si, zero-background sample holder. A typical x-ray diffraction pattern, where all major peaks are present, is shown in Fig. 1. However, when studied by powder x-ray diffraction, the powder x-ray patterns for plate-like and blade-like crystals are identical. As determined by back reflection Laue diffraction, the direction perpendicular to the face of the crystal is the $a^*$ direction, which is perpendicular to $b$ and $c$.

Back reflection Laue images were collected at room temperature. The incident x rays were produced by a 40 kV and 15 mA power source through a 0.5 mm diameter circular aperture and collected over 300 s. Crystal systems with a monoclinic unit cell (Fig. 9 in the Appendix), like La$_5$Co$_2$Ge$_3$, are part of the $2/m$ Laue class. As such, they will exhibit twofold symmetry in the back reflection pattern, which is shown in the inset to Fig. 1. Using this image and the corresponding unit cell data (Table I in the Appendix), the peaks were indexed with the assistance of CLIP (the Cologne Laue indexation program) [12] and the specific orientation of the crystal that would give rise to the resultant peaks was identified.

*Present Address: Department of Physics, University of Arizona, Tucson, AZ 85721, USA; tkong@email.arizona.edu

(2020 American Physical Society)
DC magnetization measurements were performed in a Quantum Design Magnetic Property Measurement System 3 (MPMS 3), superconducting quantum interference device (SQUID) magnetometer ($T = 1.8–300$ K, $H_{\text{max}} = 70$ kOe). All samples were manually aligned to measure the magnetization along the desired axis. A bladelike crystal was selected with measurements performed perpendicular to the face of the blade and parallel to the face of the blade. Measurements conducted perpendicular to the blade are perpendicular to the $b$-$c$ plane (i.e., parallel to $a^\prime$). Samples which were aligned parallel to the plate are in either the $b$ or $c$ direction (see Fig. 1). For measurements with $H \parallel b$ or $c$, the sample was mounted on a quartz rod and attached by GE varnish.

Resistivity measurements were performed using a standard four-probe technique with the temperature environment provided by a PPMS with $I = 1$ mA supplied by an LR-700 resistance bridge. As shown in Fig. 1, platelike samples allowed for the creation of samples that had current along the $b$ or the $c$ axis. Epotek-H20E epoxy was used to connect Pt wires to the sample so that the current was flowing in the desired direction.

Specific heat measurements between $T = 1.8$ and $50$ K were performed in a Quantum Design Physical Property Measurement System (PPMS) utilizing the relaxation technique with fitting of the whole temperature response of the microcalorimeter. A platelike sample was mounted on the microcalorimeter platform using a small amount of the Apiezon N grease. A 2% temperature rise at each measurement point was used. The addenda (contribution from the grease and sample platform) was measured separately and subtracted from the data using PPMS software.

The Zero-field muon spin rotation ($\mu$SR) measurements were performed at the $\pi$E1 beamline by using Dolly spectrometer (Paul Scherrer Institute, PSI Villigen, Switzerland). The $^4$He cryostat equipped with the $^3$He inset (base temperature $\approx 0.26$ K) was used. Samples were mounted on a thin copper foil ($\approx 10$ $\mu$m), which was transparent for positive surface muons used in our studies.

Resistivity measurements (Fig. 2) show that the samples are metallic; at $T = 300$ K, $\rho_b = 220$ $\mu$ cm, and $\rho_c = 390$ $\mu$ cm. The crystals that were measured have residual resistance ratios [RRR = $\rho(300$ K)/$\rho(2$ K)] ranging from 3–5. Below $T = 4$ K there is a sharp drop in resistivity with an onset temperature, $T_C = 3.8$ K, indicated by the arrows in the inset of Fig. 2.

The temperature-dependent magnetic susceptibility, $\chi \equiv M/H$, for La$_5$Co$_2$Ge$_3$ is shown in Fig. 3. The low temperature, $H = 50$ Oe, $M/H$ data (Fig. 3, inset) show a clear transition below 4.0 K. At the higher temperature, $H = 1$ kOe, magnetic susceptibility data manifest a clear Curie-Weiss-like behavior that can be described by

$$\frac{M}{H} = \frac{C}{T - \Theta} + \chi_0, $$

where $C$ is the Curie Constant defined as $C = N(\mu_{\text{eff}}\mu_B)^2/3k_B$, $\Theta$ is the Weiss temperature arising from interactions between spins, $\chi_0$ is a $T$-independent contribution. When fitting the temperature-dependent $M/H$ data for $20$ K $\leq T \leq 100$ K, values of $\mu_{\text{eff}} = 1.2 \mu_B$/Co, $\Theta = 0.5$ K, $\chi_0 = 0.007$ emu mol$^{-1}$ Co$^{-1}$, $\mu_{\text{eff}} = 1.0 \mu_B$/Co, $\Theta = -13$ K, $\chi_0 = 0.008$ emu mol$^{-1}$ Co$^{-1}$, and $\mu_{\text{eff}} = 1.1 \mu_B$/Co, $\Theta = 1.3$ K, $\chi_0 = 0.007$ emu mol$^{-1}$ Co$^{-1}$ were found for $H$ parallel to the $a^\prime$, $b$, and $c$ directions, respectively. Uncertainties for $\mu_{\text{eff}}$ and $\Theta$ are determined to be $\pm 0.1 \mu_B$/Co and $\pm 4$ K respectively, due primarily to the uncertainties in the measurement of the mass. For all directions, Curie-Weiss fits result in a high-temperature
paramagnetic effective moment $\mu_{\text{eff}} \sim 1.1 \mu_B/\text{Co}$. The positive (negative) sign of Weiss temperature $\Theta$ indicates dominating ferromagnetic (antiferromagnetic) interactions. In addition, a crossing of $M/H$ curves measured with field applied along different directions is observed at $\sim 40 \text{ K}$. This is due to the combination that $\chi(0)$ for $H||b$ is larger than those for $H||a^*$, $c$, and that the two curves (with $H||a^*$, $c$) with very small positive $\Theta$ values rising faster than the curve (with $H||b$) with a larger, negative $\Theta$ value. $M(T)$ data collected on a significantly larger, polycrystalline sample, measured in a 64 kOe applied field (see Fig. 10 in the Appendix), gave values of $\mu_{\text{eff}} = (1.10 \pm 0.05) \mu_B/\text{Co}$ and $\Theta = (-10.7 \pm 0.2) \text{ K}$ from a fit for $10 \text{ K} \leq T \leq 300 \text{ K}$.

Anisotropic magnetization versus field data (Fig. 4) were taken for $|H| \leq 70 \text{ kOe}$ at $T = 2 \text{ K}$. A striking anisotropy is readily apparent. Whereas for $H||a^*$ and $H||c$ there is a low-field saturation to an $\approx 0.1 \mu_B$ per mol Co value, for $H||b$, the $M(H)$ data have no such feature. For fields well above their initial saturations, the $H||a^*$ and $H||c$ $M(H)$ data show a very similar, gradual increase with $H$ as does the $H||b$ data. The inset to Fig. 4 shows that for the two easier axes there is clear hysteresis that can be associated with domain pinning. Utilizing a linear fit of the data just above saturation to extrapolate to $H = 0$, we obtain $\mu_{\text{sat}} = 0.08 \mu_B$ per mol Co, $\mu_{\text{sat}} = 0 \mu_B$ per mol Co, and $\mu_{\text{sat}} = 0.05 \mu_B$ per mol Co for the $a^*$, $b$, and $c$ directions, respectively.

Taken as a whole, the $M(T, H)$ data shown in Figs. 3 and 4 suggest that below $T_C$, La$_5$Co$_2$Ge$_3$ becomes a small moment, easy-plane ferromagnet that has a more isotropic, nonlinear, but smoothly varying $M(H)$ behavior superimposed on top of the low-field saturation.

Specific heat data, as shown in Fig. 5, exhibit a cusp with a maxima at $T = 3.8 \text{ K}$. Given that our resistivity data show a similar transition at $3.8 \text{ K}$ and our low-field $M(T)$ data show a sharp rise around $3.9 \text{ K}$, we conclude that La$_5$Co$_2$Ge$_3$ becomes ferromagnetic below $T_C = (3.8 \pm 0.1) \text{ K}$. Specific heat data were fit using $C = \gamma T + \beta T^3$ over the region $10 \text{ K} < T < 15 \text{ K}$ which is linear in $C/T$ versus $T^2$. Through this fit, we obtain coefficients of $\gamma \approx 40 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\beta \approx 2.7 \text{ mJ mol}^{-1} \text{ K}^{-4}$. We then used these fitted values of $\gamma$ and $\beta$ to extrapolate data points to $T = 0 \text{ K}$ and to estimate the electron and phonon contributions to the specific heat (shown as a red line in the figure). To estimate the entropy associated with the magnetic transition, we subtracted the inferred electron and phonon contributions from the specific heat data and integrated with respect to $T$. The entropy inferred from the specific heat data (inset of Fig. 5) reveals the total magnetic entropy of the transition is roughly $0.05R \ln(2)$ per Co.

Taken together, the data so far strongly suggest that La$_5$Co$_2$Ge$_3$ is a small moment ferromagnet; in order to test this microscopically, we performed $\mu$SR measurements on a
FIG. 6. Zero-field μSR spectra data of La$_5$Co$_2$Ge$_3$. Solid lines are fits made with two cosine signals with zero initial phase.

Sample in the 0.26 K $\leq T \leq$ 5 K temperature range (Figs. 6, 7, and 12). (See Appendix for details of μSR measurements and analysis). For $T < 4$ K, we found static magnetic order. The magnetic order is found to be commensurate, as the fit in Fig. 6 was made with two cosine signals with zero initial phase. The presence of two internal fields suggests the presence of two sites within the crystal lattice where the muons come into $\sim$20% of muons stop in a higher field site and $\sim$80% stop in a lower field site (Fig. 7).

Although La$_5$Co$_2$Ge$_3$ does order magnetically, we do not observe internal fields consistent with full Co moments (see Fig. 7). The larger internal field $B_{\text{int},1}$ only reaches 150 Oe, which is approximately one order of magnitude smaller than expected for full Co moments [13]. Such low field for the full Co moment might be expected only for highly symmetric muon stopping site, which is normally not a case for real systems. Thus, the obtained internal fields results are consistent with our small saturated moment (Fig. 4) and $\Delta S \simeq 0.05 R \ln(2)$ per Co (Fig. 5). Both of the internal fields exhibit similar temperature dependencies; when fitting the data in Fig. 7 to the power law $B = B_0(1 - (T/T_C)^{\alpha})^\beta$, we find that $\beta = 0.293$ which is consistent with three-dimensional magnetic order ($\beta_{3D} = 1/3$).

The difference between the effective moment inferred from magnetization versus temperature data (Fig. 3) and the low-field saturated moment from magnetization versus field data (Fig. 4) can be understood by considering the Rhodes-Wohlfarth ratio $q_c/q_s$ [2,8,14], where

$$\begin{align*}
q_c/qs &= (-1 + \sqrt{1 + (\mu_{\text{eff}}/\mu_B)^2})/(\mu_{\text{sat}}/\mu_B). \\
\mu_{\text{eff}} &= q_c (q_c + 2) \mu_B, \\
\mu_{\text{sat}} &= q_s \mu_B.
\end{align*}$$

We can compare La$_5$Co$_2$Ge$_3$ to other itinerant magnetic systems as shown in Fig. 8. The Rhode-Wohlfarth ratio $q_c/q_s$ can be thought of as a measure of the change in magnetic moment as you change temperature ($\mu_{\text{eff}}$ inferred from the high-temperature data, $\mu_{\text{sat}}$ inferred from the low-temperature data). For La$_5$Co$_2$Ge$_3$, $q_c/q_s = 4.9$. Figure 8 shows La$_5$Co$_2$Ge$_3$ is an intriguing combination of an ordered, line compound and one of the lowest Curie temperatures for transition-metal based ferromagnetism.

The thermodynamic, transport, and microscopic data presented on La$_5$Co$_2$Ge$_3$ all suggest that below 3.8 K there is small moment, itinerant, ferromagnetic ordering. The low-temperature, linear specific heat coefficient, $\gamma$, is also consistent with this. $\gamma = 40 \text{ mJ mol}^{-1} \text{ K}^{-2}$ is a
La$_5$Co$_2$Ge$_3$ were collected at room temperature using a γ = 50 mJ mol$^{-1}$ K$^{-2}$ (yielding a fairly standard 1 mJ mol$^{-1}$ value). Using a similar 1 mJ mol$^{-1}$ value of γ, which has a spin-density wave type of itinerant ordering near 9 K and a γ value of 20 mJ mol$^{-1}$ K$^{-2}$ (yielding a fairly standard 1 mJ mol$^{-1}$ value), a structural model containing five La, two Co, and three Ge independent atomic positions and equivalent isotropic displacement parameters.

The structure of La$_5$Co$_2$Ge$_3$ is part of a R$_5$Co$_2$Ge$_3$ family and represents a new structural type, with Pearson symbol of mS40. This structure type has been previously reported by Lin et al. [11]. The y coordinates for all atoms in this structure equal to zero, meaning that atoms in this structure are located either on planes at $y = 0$ or $y = 1/2$ arising from the C center in space group C2/m. The structure appears as the ethylenelike Co$_2$Ge$_4$ fragments and the polyacenelike ribbons immersed in a sea of the rare-earth ions, cf. Fig. 9. In this structure, Co-Co and Co-Ge bonds show the strongest covalent bonding interactions, as indicated by respective bond distances (dCo$_2$Ge$_4$ = 2.325–2.358 Å).

TABLE I. Crystal data and structure refinement for La$_5$Co$_2$Ge$_3$.

| Parameter                  | Value            |
|----------------------------|------------------|
| Empirical formula          | La$_5$Co$_2$Ge$_3$ |
| Formula weight             | 1030.2 g/mol     |
| Space group, Z             | C2/m, 4          |
| Unit cell dimensions       |                 |
| $a$                        | 18.354(4) Å     |
| $b$                        | 4.3479(9) Å     |
| $c$                        | 13.279(3) Å     |
| $\beta$                    | 109.592(2)$^\circ$ |
| Z                          | 4                |
| Density (calculated)       | 6.663 g/cm$^3$  |
| Reflections collected      | 30592 [R(int) = 0.0384] |
| Data / restraints / parameters | 5893 / 0 / 62 |
| Goodness-of-fit on F$^2$   | 1.179            |
| Final R indices [I > 2σ(I)]|                  |
| $R_1$                      | 0.0342           |
| $wR_2$                     | 0.0530           |
| $R$ indices (all data)     | 0.0512           |
| $wR_2$                     | 0.0564           |
| Largest diff. peak and hole| 1.316 and $-1.486$ e Å$^{-3}$ |

We would like to thank A. Kreyssig for useful discussions and R. A. Ribeiro for assistance with magnetization measurements. This work is supported by the US DOE, Basic Energy Sciences under Contract No. DE-AC02-07CH11358 and the Gordon and Betty Moore Foundation’s EPiQS Initiative through Grant No. GBMF4411.

APPENDIX A: STRUCTURE REFINEMENT

Single crystal x-ray diffraction intensity data for La$_5$Co$_2$Ge$_3$ were collected at room temperature using a Bruker SMART APEX II diffractometer (Mo K$_\alpha$ radiation, $\lambda = 0.71073$ Å). Data reduction, integration, unit cell refinements, and absorption corrections were done with the aid of subprograms in APEX2 [20,21]. Space group determination, Fourier synthesis, and full-matrix least-squares refinements on F$^2$ were carried out by in SHELXTL 6.1 [22]. The direct methods in space group C2/m yielded a structural model equal to zero, meaning that atoms in this structure are located either on planes at $y = 0$ or $y = 1/2$ arising from the C center in space group C2/m. The structure appears as the ethylenelike Co$_2$Ge$_4$ fragments and the polyacenelike ribbons immersed in a sea of the rare-earth ions, cf. Fig. 9. In this structure, Co-Co and Co-Ge bonds show the strongest covalent bonding interactions, as indicated by respective bond distances (dCo$_2$Ge$_4$ = 2.325–2.358 Å).

TABLE II. The refined atomic positions and equivalent isotropic displacement parameters for La$_5$Co$_2$Ge$_3$.

| Atom | Wyck. | Symm. | x    | y    | z    | $U_{eq}$ (Å$^2$) |
|------|-------|-------|------|------|------|------------------|
| La1  | 4i    | m     | 0.0013(1) | 0    | 0.1371(1) | 0.0015(1) |
| La2  | 4i    | m     | 0.3171(1) | 0    | 0.4397(1) | 0.0015(1) |
| La3  | 4i    | m     | 0.3228(1) | 0    | 0.1090(1) | 0.0014(1) |
| La4  | 4i    | m     | 0.4998(1) | 0    | 0.3616(1) | 0.0015(1) |
| La5  | 4i    | m     | 0.6819(1) | 0    | 0.2300(1) | 0.0014(1) |
| Co1  | 4i    | m     | 0.0670(1) | 0    | 0.5212(1) | 0.0017(1) |
| Co2  | 4i    | m     | 0.5661(1) | 0    | 0.0240(1) | 0.0019(1) |
| Ge1  | 4i    | m     | 0.1325(1) | 0    | 0.7121(1) | 0.0015(1) |
| Ge2  | 4i    | m     | 0.1323(1) | 0    | 0.3749(1) | 0.0015(1) |
| Ge3  | 4i    | m     | 0.1466(1) | 0    | 0.0493(1) | 0.0015(1) |
dCo − Ge = 2.494–2.558 Å). Notably, the separations for La1-La4, La2-La4, and La4-La4 pairs are smaller than the sum of Pauling’s metallic radii (3.648 Å) [23], suggesting considerable covalent interactions among them. These pairs form two-dimensional honeycomb nets parallel to the bc plane, hexagons in the net are perpendicularly penetrated by Co-Co bonds (Fig. 1). Sandwiched by the foregoing honeycomb nets, La2, La3, and La5 atoms form slabs of edge-sharing tetrahedra with slightly longer La-La distances (3.647–3.924 Å).

**APPENDIX B: MAGNETIZATION MEASUREMENT AND ANALYSIS ON POWDER SAMPLE**

In order to better measure the high-temperature Curie-Weiss behavior, a powder sample was made by grinding 95 mg of single crystals and was measured in a field of 64 kOe as a function of temperature. The temperature-dependent 

\[ H/M \] data (Fig. 10, inset) demonstrate that the \( \chi_0 \) term is relatively large over the whole temperature range and does not allow for insightful use of such plots.

**APPENDIX C: ITINERANT FERROMAGNETISM ANALYSIS BY SPIN-FLUCTUATION THEORY**

The itinerant nature of the ferromagnetism can be further analyzed by using Takahashi’s spin-fluctuation theory for weak (small ordered moment) itinerant ferromagnets [24,25]. In Takahashi’s theory, to capture the spin fluctuation, the expansion of the free energy \( F(M, T) \) for a ferromagnet is kept up to sixth order,

\[
F(M, T) = F(0, T) + \frac{1}{2}a_2(T)M^2 + \frac{1}{4}a_4(T)M^4 + \frac{1}{6}a_6(T)M^6 - MH, \tag{C1}
\]

where the prefactors \( a_2(T) \) and \( a_6(T) \) are related to the spin fluctuation. Minimizing free energy gives

\[
H = a_2(T)M + a_4(T)M^2 + a_6(T)M^5. \tag{C2}
\]

For the ground state (\( T = 0 \) K), one considers the expansion of \( F(M, T) \) up to fourth order and obtains

\[
H = \frac{F_1}{(g\mu_B)^2N_0}(M^2 - M_0^2)M, \tag{C3a}
\]

\[
F_1 = \frac{2k_B T_A^2}{15cT_0}, \tag{C3b}
\]

where \( c = 1/2 \) is a constant, \( N_0 \) is the number of magnetic atoms, \( M_0 \) is the ordered moment in the ground state, \( T_0 \) and \( T_A \) (in the temperature units K) are the ferromagnetic spin fluctuation parameters which measure the energy width and wave vector width of the spin fluctuation, respectively. Thus, in the ground state, the magnetic isotherm is influenced by the zero-point spin fluctuation \( F_1 \), which depends on the ferromagnetic spin fluctuation parameters \( T_0 \) and \( T_A \). These two parameters can be inferred from magnetic isotherm data:

\[
M^2 = \frac{1}{(248.20 \text{ emu mol}^{-1} \text{ Co}^{-1})^2} \frac{H}{M} + M_0^2, \tag{C4a}
\]

\[
M_0 \approx 2 \left( \frac{C_{4/3} S T_0}{T_A} \frac{T_C}{T_A} \right)^{2/3}, \tag{C4b}
\]

where \( C_{4/3} \) is a constant \( \sim 1 \). Based on Eqs. C3(a) and 5(b), \( T_0 \) and \( T_A \) can be calculated from the slopes and intercepts of \( M^2 \) versus \( H/M \) plots (Arrrott plot) at low temperatures (where \( M^2 \) versus \( H/M \) is linear at high fields) [26], given that \( T_C \) is known (or can be also determined from Arrott plots).

For the temperatures close to \( T_C \), the magnetic isotherms are predominately influenced by temperature-induced spin fluctuation \( [a_6 \text{ term in Eq. (C2)}] \) instead of zero-point spin fluctuation. At \( T_C \), \( a_2 \) and \( a_4 \) are zero and Eq. (C2) can be expressed as

\[
\frac{M^4}{H/M} = \frac{1}{(4.671 \text{ emu mol}^{-1} \text{ Co}^{-1})(\frac{T_T}{T_C})}. \tag{C5}
\]
In this case, isotherm $M^4$ versus $H/M$ is linear and the slope can be obtained. $T_0$ and $T_A$ parameters can then be calculated based on Eqs. (C4b) and (C5).

Now we apply this analysis to our measurement results. $M(H)$ curves are measured at 2 K with field $H$ applied along different directions. In the following, we take the $M(H)$ data with $H||a^*$ (largest magnetization direction) to estimate the spin fluctuation. Figures 11(a) and 11(b) present the $M$ at 2 K of La$_5$Co$_2$Ge$_3$ for magnetic field $H$ and the determined internal fields ($B$) at 2 K and the obtained slope is 1.56 $\times 10^{-9}$ ($\mu_B$/mol-Co$^2$).

In the following, we estimate the ordered magnetic moment in the ground state, $M_0$, based on the magnetization at 2 K and the determined internal fields ($B_1$, $B_2$) behavior from $\mu$SR measurements. Magnetization at 2 K, $M_{2K}$, is obtained to be 0.08 $\mu_B$/mol-Co for $H||a^*$ (see Fig. 4). Since internal field $B$ is directly proportional to magnetization $M$ and follows $B = B_0(1 - (T/T_C)^{\alpha})^\beta$, where $\alpha = 2.666$ and $\beta = 0.293$ are determined from $\mu$SR measurements, the temperature-dependent magnetization can be described as $M = M_0(1 - (T/T_C)^{\alpha})^\beta$. From this, $M_0$ is calculated to be 0.085 $\mu_B$/mol-Co.

With the slope of $M^4/M_0$ and $M_0$, the fluctuation parameters are calculated to be $T_0 = 2227$ K and $T_A = 1257$ K based on Eqs. (C4b) and (C5). The ratio $T_C/T_0$ characterizes the degree of itinerancy. La$_5$Co$_2$Ge$_3$ gives a $T_C/T_0$ value of 0.0017, indicating strong itinerant nature of the magnetism. In the end, we point out that to better investigate the magnetism of La$_5$Co$_2$Ge$_3$ in the spin-fluctuation theory, further detailed measurements of $M(H)$ isotherms over a wider range of temperatures and orientations would be needed to refine our values of $T_0$ and $T_A$ to further explore this model [24,25].

APPENDIX D: ZF $\mu$SR DATA ANALYSIS PROCEDURE

The time evolution of the muon spin polarization $P(t)$ due to interaction with sample was described by assuming the presence two internal fields $B_{int,1}$ and $B_{int,2}$ with the corresponding weight $f$ and $(1-f)$, respectively. In the case of La$_5$Co$_2$Ge$_3$, the presence of two internal fields most probably corresponds to the two muon-stopping sites. Given the rather large and complex unit cell of La$_5$Co$_2$Ge$_3$ (Fig. 9) this is not all surprising and the presence of multiple muon sites is often observed (see, e.g., Refs. [27–29] and references therein). The following functional form was used:

$$P(t) = \frac{1}{3} e^{-\lambda_T t} + \frac{\lambda_T}{\lambda_L} \left( f e^{-\lambda_T t} + (1-f) e^{-\gamma_{\mu} B_{int,1} t} \right).$$

Here, $\gamma_{\mu} = 2\pi 135.5$ MHz/T is the muon gyromagnetic ratio, and $\lambda_T$ and $\lambda_L$ are the transverse and the longitudinal exponential relaxation rates, respectively. The occurrence of 2/3 oscillating and 1/3 nonoscillating $\mu$SR signal fractions originates from the spatial averaging in powder samples, where 2/3 of the magnetic field components are perpendicular to the muon spin and cause a precession, while the 1/3 longitudinal field components do not. Note that Eq. (D1) only describes the contribution from the sample. The background contribution, which is not included in the equation, corresponds to muons stopped outside of the sample (sample
holder, cryostat walls, cryostat windows, glue, etc.). During the fit, the background contribution was described by a simple exponential relaxation function as $e^{-\lambda_{BG}t}$, where $\lambda_{BG}$ is a temperature independent relaxation rate $\sim \text{ms}^{-1}$. The substantial background is the feature of all low-temperature cryostats, which depends not only on the cryostat, but also on the sample size and the amount of glue used. A fully magnetic sample in this case suggests approximately 65% sample and 35% background contributions, respectively. These numbers are quite reasonable for the amount of the sample used in our studies.

The weight of the high-field component ($f$) is field independent and was found to be $f \lesssim 0.19$. Temperature evolutions of the transversal ($\lambda_{T,1}$ and $\lambda_{T,2}$) and longitudinal relaxation ($\lambda_{L}$) are presented in Fig. 12. The similar temperature dependencies of $B_{\text{int},1}$ and $B_{\text{int},2}$ (see Fig. 7 in the main text) as well as $\lambda_{T,1}$ and $\lambda_{T,2}$ (see Fig. 12) confirms the presence of two muon-stopping sites in La$_5$Co$_2$Ge$_3$.

[1] A. Szytula and J. Leciejewicz, Handbook of Crystal Structures and Magnetic Properties of Rare Earth Intermetallics (CRC, Boca Raton, Florida, 1994).
[2] B. T. Matthias, A. M. Clogston, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. Lett. 7, 7 (1961).
[3] B. T. Matthias and R. M. Bozorth, Phys. Rev. 109, 604 (1958).
[4] K. Kadowaki, K. Okuda, and M. Date, J. Phys. Soc. Jpn. 51, 2433 (1982).
[5] M. Avila, S. Bud’ko, and P. Canfield, J. Magn. Magn. Mater. 270, 51 (2004).
[6] T. Fujiwara, N. Aso, H. Yamamoto, M. Hedo, Y. Saiga, M. Nishi, Y. Uwato, and K. Hirota, J. Phys. Soc. Jpn. 76, 60 (2007).
[7] E. Svanidze, J. K. Wang, T. Besara, L. Liu, Q. Huang, T. Siegrist, B. Frandsen, J. W. Lynn, A. H. Nevidomskyy, M. B. Gamza et al., Nat. Commun. 6, 7701 (2015).
[8] P. Rhodes and E. Wohlfarth, Proc. R. Soc. London A 273, 247 (1963).
[9] P. C. Canfield and I. R. Fisher, J. Cryst. Growth 225, 155 (2001).
[10] P. C. Canfield, Rep. Prog. Phys. 83, 016501 (2020).
[11] Q. Lin, K. Aguirre, S. M. Saunders, T. A. Hackett, Y. Liu, V. Tafour, D. Paudyal, S. Bud’ko, P. C. Canfield, and G. J. Miller, Chem. - Eur. J. 23, 10516 (2017).
[12] O. J. Schumann, Cologne Laue Interference Program (CLIP) (2009), http://clip4.sourceforge.net/manual.pdf.
[13] L. de Jongh and A. Miedema, Adv. Phys. 23, 1 (1974).
[14] J. M. Santiago, C.-L. Huang, and E. Morosan, J. Phys.: Condens. Matter 29, 373002 (2017).
[15] S. Jia, S. L. Bud’ko, G. D. Samolyuk, and P. C. Canfield, Nat. Phys. 3, 334 (2007).
[16] V. Tafour, U. S. Kaluarachchi, R. Khasanov, M. C. Nguyen, Z. Guguchia, P. K. Biswas, P. Bonfà, R. D. Renzi, X. Lin, S. K. Kim et al., Phys. Rev. Lett. 117, 037207 (2016).
[17] U. S. Kaluarachchi, L. Xiang, J. Ying, T. Kong, V. Struzhkin, A. Gavriliiu, S. L. Bud’ko, and P. C. Canfield, Phys. Rev. B 98, 174405 (2018).
[18] U. S. Kaluarachchi, V. Tafour, S. L. Bud’ko, and P. C. Canfield, Phys. Rev. B 97, 045139 (2018).
[19] M. Brando, D. Belitz, F. Gro sche, and T. Kirkpatrick, Rev. Mod. Phys. 88, 025006 (2016).
[20] SMART for Windows NT/2000. Version 6.148, Bruker AXS Inc., Madison WI, USA (2013).
[21] SAINT plus. Version 8.30, Bruker AXS Inc., Madison WI, USA (2002).
[22] SHELXTL, 6.10 ed., Bruker Analytical X-ray Systems, Inc., Madison WI (2000).
[23] L. Pauling, The Nature of the Chemical Bond, 3rd ed. (Cornell University Press, Ithaca, NY, 1960), p. 644.
[24] T. Moriya and Y. Takahashi, J. Phys. Soc. Jpn. 45, 397 (1978).
[25] Y. Takahashi, Spin Fluctuation Theory of Itinerant Electron Magnetism (Springer, Berlin, Heidelberg, 2013).
[26] A. Arrott, PR 108, 1394 (1957)
[27] A. Amato, P. Dalmas de Réotier, D. Andreica, A. Yaouanc, A. Suter, G. Lapertot, I. M. Pop, E. Morenzoni, P. Bonfà, F. Bernardini, and R. De Renzi, Phys. Rev. B 89, 184425 (2014).
[28] R. Khasanov, A. Amato, P. Bonfà, Z. Guguchia, H. Luetkens, E. Morenzoni, R. De Renzi, and N. D. Zhigadlo, Phys. Rev. B 93, 180509(R) (2016).
[29] R. Khasanov, A. Amato, P. Bonfà, Z. Guguchia, H. Luetkens, E. Morenzoni, R. De Renzi, and N. D. Zhigadlo, J. Phys.: Condens. Matter 29, 164003 (2017).