Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis of $ThCr_2Si_2$-type arsenides from Bi flux

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Experimental Details

Starting materials. Finely dispersed powders of lanthanum (99.9%) and arsenic (99.99%), as well as bismuth granules (99.997%), were obtained from Alfa Aesar and used as received. Cobalt powder (Alfa Aesar, 99.5%) was additionally purified by heating under a flow of H_2 gas at 775 K for 5 h. All manipulations during sample preparation were carried out in an argon-filled dry box (content of $O_2 <$ 1 ppm).

Synthesis. Method 1. For the preparation of $LaCo_2As_2$, elements were mixed in the La:Co:As = 1:2:2 ratio (total mass = 0.25g) and compressed into a pellet. The pellet was arc-melted under argon atmosphere and the obtained ingot was sealed under vacuum ($< 10^{-2}$ mbar) in a 10 mm i.d. silica tube. The ingot was annealed at 1173 K for 2 weeks and ground to powder. Powder X-ray diffraction analysis showed that this method resulted in a mixture of LaAs, $LaCo_2As_2$, and La_2O_3, as well as a trace amount of CoAs (Fig. S1b). The presence of La_2O_3 is explained by oxidation of unreacted La. This impurity is not observed in preparations from metal flux (see Method 3), because La_2O_3 dissolves in dilute acid during the workup procedure.

Method 2. For the preparation of CoAs, powders of cobalt and arsenic powders were mixed in the 1:1 ratio and compressed into a pellet under argon atmosphere. The pellet was sealed under vacuum ($< 10^{-2}$ mbar) in a 10 mm i.d. silica tube and annealed at 823 K for 2 days, followed by re-grinding, pressing again into a pellet, and annealing at 1073 K for 8 days. The pellet was ground to powder and the phase purity was confirmed by powder X-ray diffraction. For the preparation of $LaCo_2As_2$, powders of La and CoAs were mixed in the 1:2 ratio (total mass = 0.25g) and compressed into a pellet under argon atmosphere. The pellet was sealed under vacuum ($< 10^{-2}$ mbar) in a 10 mm i.d. silica tube and annealed at 1323 K for 2 weeks. The annealed pellet was ground to powder, and the phase purity was checked by powder X-ray diffraction, which showed that this method resulted in $LaCo_2As_2$ as a major product and trace impurities of CoAs and La_2O_3 (Fig. S1c). The sample was further re-ground and re-annealed at 1323 K for 2 weeks, and then this procedure was repeated once again. This resulted in an increased amount of $LaCo_2As_2$.

Method 3. Synthesis in Bi flux. The starting materials were mixed in the La:Co:As:Bi = 1:2:2:30 ratio (total mass = 5 g) in a 10 mm i.d. silica tube, which was sealed under vacuum ($< 10^{-2}$ mbar). The mixture was annealed at 1173 K for 10 days and quenched into water. The Bi flux was removed by soaking the samples in a mixture of glacial acetic acid and 30% H_2O_2 (1:1 v/v) for 2-3 days, and the sample was washed with dilute HCl (1:1 v/v) and water. The phase purity was confirmed by powder X-ray diffraction. A slight discrepancy in the relative intensity of observed and calculated reflections (Fig. 2) arises from the preferential ordering of crystallites, which generally have square-pyramidal shapes. Single-crystal X-ray structure determination revealed that the composition of obtained material is $La_{0.969(4)}Bi_{0.031(4)}Co_{1.91(1)}As_2$.

Physical measurements. Powder X-ray diffraction was performed on a Rigaku DMAX 300 Ultima III powder X-ray diffractometer using Cu$K\alpha$ radiation (λ = 1.54185 Å) and on an original X-ray diffraction setup using Guinier camera 670 with a Huber imaging plate and a Ge crystal monochromator (Cu$K\alpha_1$, λ = 1.54060 Å). For the accurate refinement of the unit cell, elemental Ge was used as an internal standard. The unit cell parameters were calculated by least-squares fitting with the WinCSD software package.[S1] Elemental analysis of select single crystals was carried out on a JEOL 5900 scanning electron microscope with an energy-dispersive X-ray (EDX) microanalysis. Magnetic measurements were performed on polycrystalline samples with a Quantum Design SQUID magnetometer MPMS-XL. DC magnetic susceptibility measurements were carried out in an applied field of 0.001 T in the 1.8–300 K range. The magnetic ordering temperatures were determined as inflection points of the χ vs. T curves (Fig. 3a). Isothermal field dependences of magnetization were measured at 1.8 K with the magnetic field varying from 0 to 7 T.

Single crystal X-ray diffraction. For the room-temperature experiment, a single crystal of $La_{0.969}Bi_{0.031}Co_{1.91}As_2$ was glued with epoxy cement on the tip of a quartz fiber and mounted on a goniometer head of a Bruker AXS SMART diffractometer with an APEX-II CCD detector. The same crystal was later used for the low-temperature experiment. The crystal was suspended in Parathone-N oil (Hampton Research) and mounted on a cryoloop which was placed in an N_2 cold stream, cooled down to 130 K at 5 K/min, and allowed to equilibrate at this temperature for one hour prior to the data collection. In both cases, the data sets were recorded as ω-scans at 0.3° stepwidth and integrated with the Bruker SAINT software.[S2] All the data sets were indexed in the tetragonal body-centered unit cell. The only systematic extinctions observed corresponded to the *I*-centered lattice. An analytical absorption correction was applied using face-indexing of the crystal. Solution and refinement of the crystal structures was carried out using the SHELX suite of programs.[S3] The structures were solved in the *I*4/*mmm* space group (No. 139), and the final refinement was performed with anisotropic atomic displacement parameters for Co and As atoms. The disordered Bi and La atomic positions were refined isotropically, but constrained to have equal atomic displacement parameters. A summary of pertinent information relating to unit cell parameters, data collection, and refinements are provided in Tables S1 and S2.

Quantum-Chemical Calculations. Density functional band structure calculations using a full potential all-electron local orbital code FPLO (version fplo7.00–28) within the local (spin) density approximation (*LSDA*) were performed including spin-orbit coupling.[S4,S5] The Perdew–Wang parameterization of the exchange-correlation potentials was employed.[S6] Band structures and the density of states (DOS) were calculated after convergence of the total energy on a dense *k*-mesh with 32×32×32 points. Calculations were performed on two compounds, having the unit cells parameters of $LaCo_2As_2$ and $La_{0.969}Bi_{0.031}Co_{1.91}As_2$. For both calculations the composition $LaCo_2As_2$ was assumed with following atomic coordinates: La (0; 0; 0), Co (0; ½; ¼), As (0; 0; 0.3625), space group *I*4/*mmm* (No. 139). Calculations were performed in a spin-polarized model assuming ferromagnetic ordering of all Co magnetic moments.

The calculations revealed that the band structure remains essentially similar in both cases (Figs. S3 and S4). Therefore, the increase in T_C upon going from $LaCo_2As_2$ to $La_{0.969}Bi_{0.031}Co_{1.91}As_2$ may arise from the substitution of Bi for La and/or formation of Co vacancies, which are difficult to account for by the band structure calculations.

[S1] L. G. Akselrud, P. Y. Zavalii, Y. Grin, V. K. Pecharski, B. Baumgartner and E. Woelfel, *Mater. Sci. Forum*, 1993, **133-136**, 335-340.
[S2] SMART and SAINT; Bruker AXS Inc.: Madison, WI, USA, 2007.
[S3] G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **A64**, 112-122.
[S4] K. Koepemik and H. Eschrig, *Phys. Rev. B*, 1999, **59**, 1743-1757.
[S5] L. Ophale, K. Koepemik and H. Eschrig, *Phys. Rev. B*, 1999, **60**, 14035-14041.
[S6] J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244-13249.

Table S1. Data collection and structure refinement parameters for $La_{0.969}Bi_{0.031}Co_{1.91}As_2$.[a]

Composition	$La_{0.969(8)}Bi_{0.032(8)}Co_{1.92(1)}As_2$	$La_{0.969(4)}Bi_{0.031(4)}Co_{1.91(1)}As_2$
Crystal system	*Tetragonal*	
Space group	*I*4/*mmm* (No. 139)	
Temperature	293 K	130 K
Unit cell, Å	a = 4.0494(3) c = 10.4987(8)	a = 4.0499(5) c = 10.412(1)
V, Å^3	172.15(2)	170.77(4)
Z	2	
λ, Å	Mo$K\alpha$, 0.71073	
ρ_{calc}, g cm^{-3}	7.788	7.840
μ, mm^{-1}	41.267	41.554
$2\theta_{max}$	37.48	39.82
Refl. collected	1214	1139
R_{int}	0.021	0.023
Independ. refls.	162	189
Param. refined	11	11
R_1, wR_2, [$F_o > 4\sigma F_o$]	0.019, 0.045	0.020, 0.048
Diff. peak and hole, e/Å^3	1.404 and –3.068	2.130 and –1.795
Goodness-of-fit	1.229	1.315

[a] Further details of the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting depository numbers CSD-422569 (293 K) and CSD-422570 (130 K).

Table S2. Atomic coordinates and equivalent displacement parameters for $La_{0.969}Bi_{0.031}Co_{1.91}As_2$.

Atom	**Site**	***x/a***	***y/b***	***z/c***	***s.o.f.***	U_{eq}[a]
				293 K		
La	2*a*	0	0	0	0.969(8)	0.0052(2)[b]
Bi	4*e*	0	0	0.021(4)	0.016(4)	0.0052(2)[b]
Co	4*d*	0	½	¼	0.958(7)	0.0087(3)
As	4*e*	0	0	0.36247(6)	1	0.0087(2)
				130 K		
La	2*a*	0	0	0	0.969(4)	0.0029(1)[b]
Bi	4*e*	0	0	0.027(3)	0.0156(18)	0.0029(1)[b]
Co	4*d*	0	½	¼	0.953(6)	0.0055(2)
As	4*e*	0	0	0.36287(5)	1	0.0060(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Refined isotropically.

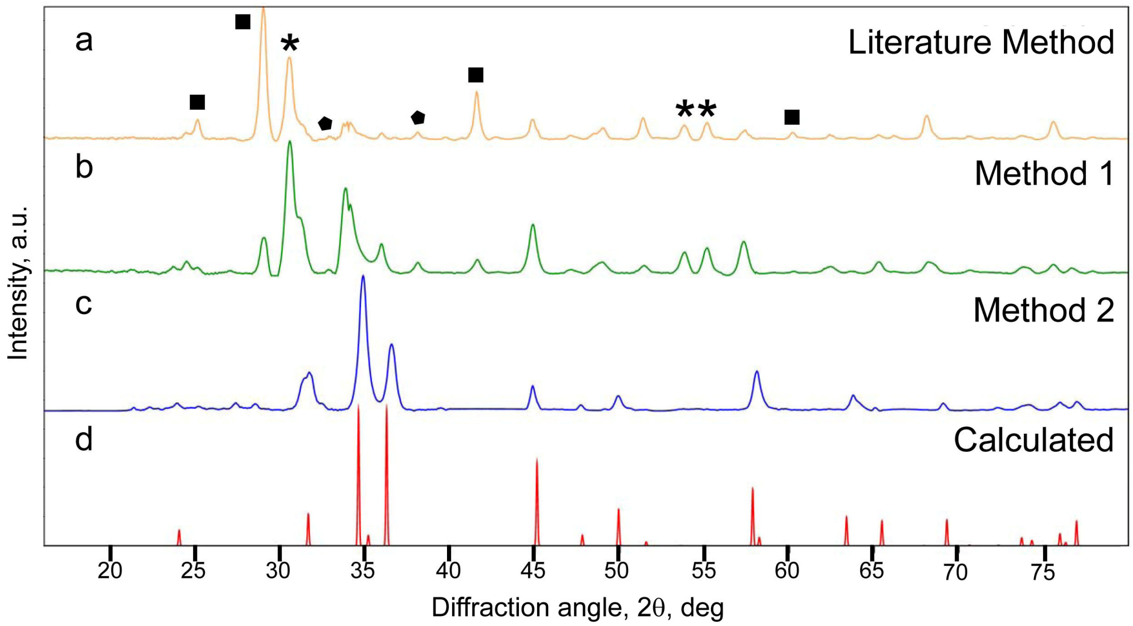

Figure S1. Powder X-ray diffraction patterns for products of reactions used to prepare $LaCo_2As_2$: (a) Literature method – annealing of a mixture of elements, according to the procedure reported by Jeitschko *et al.*; (b) Method 1 – arc melting of a mixture of elements with subsequent annealing; (c) Method 2 – annealing of a mixture of La and CoAs. (d) The calculated powder diffraction pattern of $LaCo_2As_2$. The impurities include LaAs (■) , CoAs (⬟), and La_2O_3 (*).

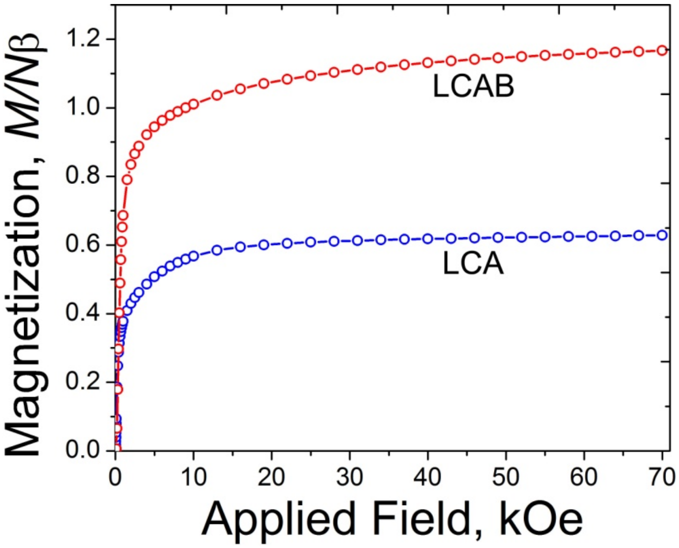

Figure S2. The isothermal field dependence magnetization curves recorded at 1.8 K for $LaCo_2As_2$ (LCA) and $La_{0.969}Bi_{0.031}Co_{1.91}As_2$ (LCAB).

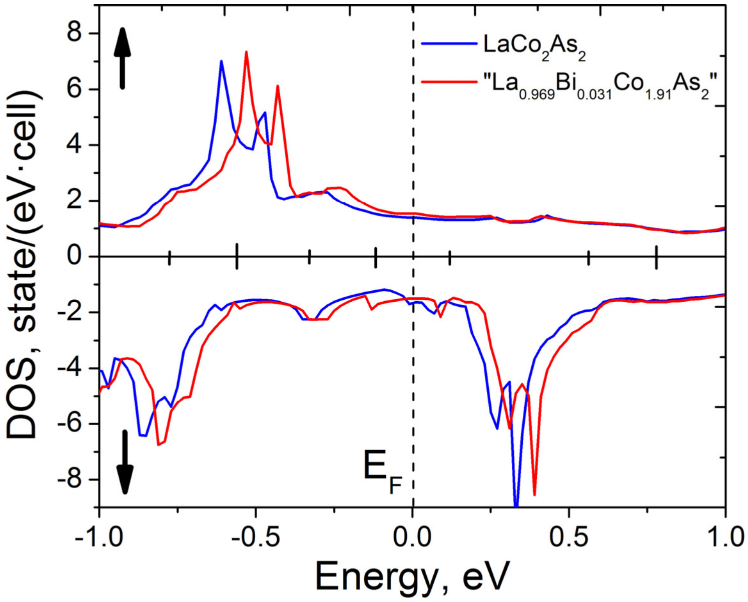

Figure S3. Spin-polarized density of states (DOS) diagram calculated for $LaCo_2As_2$ (blue curve) and "$LaCo_2As_2$" having unit cell parameters of $La_{0.969}Bi_{0.031}Co_{1.91}As_2$ (red curve).

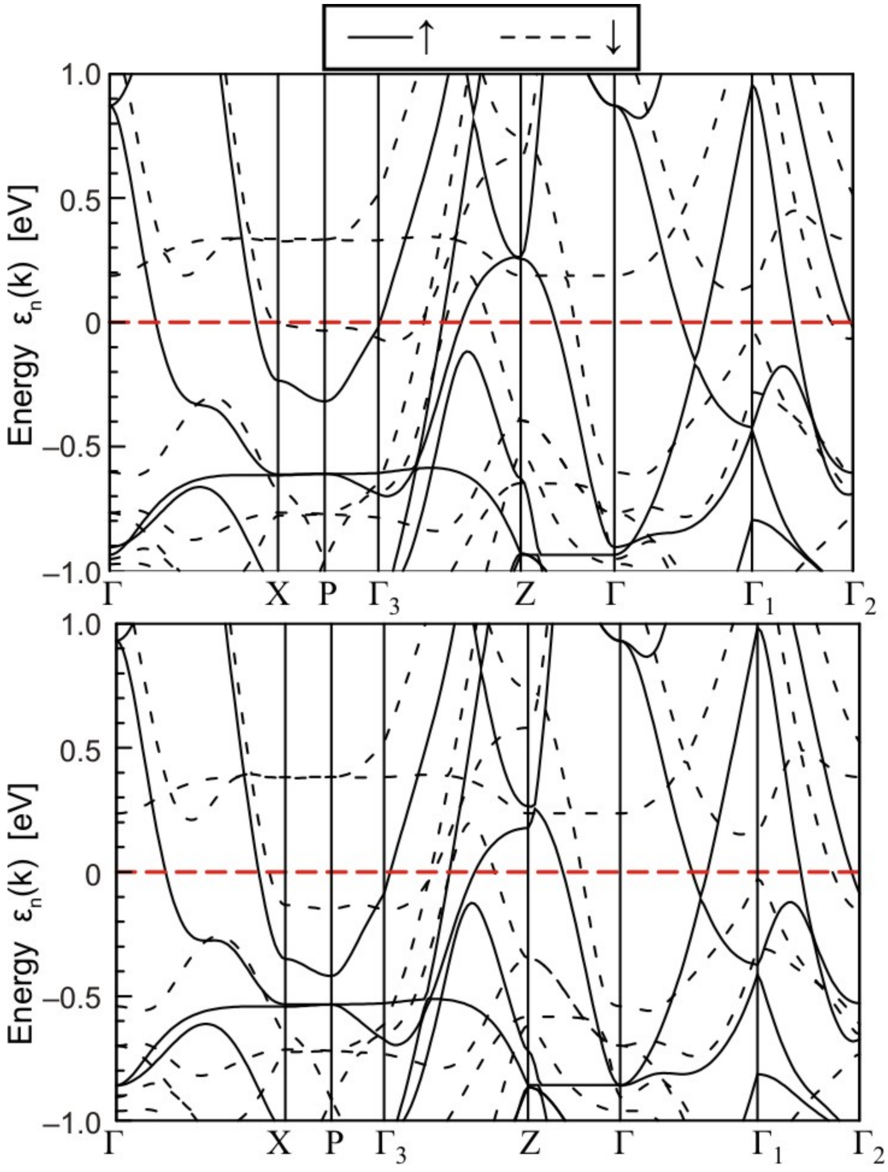

Figure S4. Spin-polarized band diagram for the ferromagnetic model of $LaCo_2As_2$ (top) and "$LaCo_2As_2$" having unit cell parameters of $La_{0.969}Bi_{0.031}Co_{1.91}As_2$ (bottom).