Synthesis, Structures, and Magnetic Properties of Rare-Earth Cobalt Arsenides, RCo$_2$As$_2$ (R = La, Ce, Pr, Nd)

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Supporting Information

ABSTRACT: Four rare-earth cobalt arsenides, RCo$_2$As$_2$ (R = La, Ce, Pr, Nd), were obtained by reactions of constituent elements in molten Bi. The use of Bi flux also allowed the growth of representative single crystals. All compounds are isostructural and belong to the ThCr$_2$Si$_2$ type (space group I4/mmm). The formation of Co vacancies is observed in all structures, while the structures of La- and Ce-containing compounds also show incorporation of minor Bi defects next to the R crystallographic site. Correspondingly, the general formula of these materials can be written as R$_{1−x}$Bi$_x$Co$_{2−δ}$As$_2$, with $x/δ = 0.03/0.1$, 0.05/0.15, 0/0.2, and 0/0.3 for R = La, Ce, Pr, and Nd, respectively. All compounds exhibit high-temperature ferromagnetic ordering of Co magnetic moments in the range 60−200 K. Electronic band structure calculations revealed a high peak in the density of states at the Fermi level, thus supporting the itinerant nature of magnetism in the Co sublattice. The magnetic ordering in the lanthanide sublattice takes place at lower temperatures, with the R moments aligning antiparallel to the Co moments to give a ferrimagnetic structure. The measurements on oriented single crystals demonstrated significant magnetic anisotropy in the ferrimagnetic state, with the preferred moment alignment along the $c$ axis of the tetragonal lattice. Neutron powder diffraction failed to reveal the structure of magnetically ordered states but confirmed the presence of Co vacancies. X-ray absorption near-edge structure spectroscopy on Ce$_{1.95}$Bi$_{0.05}$Co$_{1.85}$As$_2$ showed the average oxidation state of Ce to be +3.06. Solid state NMR spectroscopy revealed a substantially reduced hyperfine field on the Co atoms in the vicinity of Bi defects.

INTRODUCTION

Layered pnictides of the ThCr$_2$Si$_2$ structure type have drawn increasing attention due to the recent discovery of a new class of high-temperature superconductors derived from AFe$_2$As$_2$ (A = Ca, Sr, Ba, Eu).1 The superconductivity is imparted by proper electron- or hole-doping of these parent materials. For example, the substitution of K for Ba or Co for Fe suppresses antiferromagnetic (AFM) ordering in BaFe$_2$As$_2$ and results in the superconducting behavior with $T_C = 38$ K in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$3 and $T_C = 22$ K in BaFe$_{1.3}$Co$_{0.2}$As$_2$.5 At higher doping levels, the superconductivity disappears and, for instance, pure BaCo$_2$As$_2$ shows paramagnetic properties.4 Naturally, such studies of electron doping in AFe$_2$As$_2$ have sparked interest in the Co-containing analogues, ACo$_2$As$_2$. Similar to BaCo$_2$As$_2$, SrCo$_2$As$_2$ is a paramagnet but shows AFM spin fluctuations at 5 K while CaCo$_2$As$_2$ exhibits AFM ordering at ~70 K.6 In EuCo$_2$As$_2$, the AFM ordering occurs at 39 K but it has been attributed to the ordering of the Eu$^{2+}$ 4f magnetic moments rather than the Co 3d moments.7 We find, however, that with the exception of EuCo$_2$As$_2$, very little is
known about the synthesis and properties of other rare-earth containing RCo$_3$As$_2$ materials.

The investigation of RCo$_3$As$_2$ phases is interesting from the magnetism point of view, considering the rich and fascinating magnetic behavior established for isostructural RCo$_3$P$_2$. Among the latter, LaCo$_3$P$_2$ orders ferromagnetically (FM) at 132 K while other RCo$_3$P$_2$ (R = Ce, Pr, Nd, Sm) exhibit AFM ordering above room temperature. Upon doping of Pr (or Nd) for La in LaCo$_3$P$_2$, the FM ordering temperature increases from 132 to 275 K. Furthermore, the quaternary La$_{0.75}$Pr$_{0.25}$Co$_2$P$_2$ phases exhibit multiple magnetic transitions that are not observed in their ternary congeners. For example, as the temperature is lowered, La$_{0.75}$Pr$_{0.25}$Co$_2$P$_2$ undergoes FM ordering of Co 3d moments in the ab plane of the tetragonal lattice at 170 K, followed by FM ordering of Pr 4f moments along the c axis at 67 K that causes reorientation of the Co moments along the c axis in the direction antiparallel to the Pr moments. Thus, La$_{0.75}$Pr$_{0.25}$Co$_2$P$_2$ is characterized by a ferrimagnetic (FiM) ground state, not observed in any of the ternary RCo$_3$P$_2$ phases. Such drastic change in the magnetic behavior upon partial isoelectronic substitution of Pr for La is explained by the stabilization of the ferromagnetism in the Co sublattice due to subtle changes of the electronic structure at the Fermi level.

We also have shown that the substitution of Fe for Co in LaCo$_3$P$_2$ leads to the suppression of FM ordering and emergence of a spin-glass state even at low concentrations of Fe (≈10%). The influence of the pnictogen on the magnetic properties of these materials has been unknown until recently, mainly due to the lack of a reliable synthetic approach to phase-pure RCo$_3$As$_2$ samples or their representative single crystals. In fact, prior to our work, there existed only one report on the preparation of RCo$_3$As$_2$, in which the attempts to obtain single crystals from Sn flux were unsuccessful.

Recently, we have reported the successful preparation of single-phase LaCo$_3$As$_2$ and the growth of corresponding single crystals by carrying out the reaction between constituent elements in molten Bi. Similar to LaCo$_3$P$_2$, which orders FM at $T_c = 132$ K, LaCo$_3$As$_2$ shows FM ordering at $T_c \approx 200$ K. Furthermore, we established that a small amount of Bi substitutes for La with a simultaneous formation of vacancies in the Co sublattice, a structural feature not observed for RCo$_3$P$_2$ analogues. Herein, we demonstrate that the reaction in Bi flux serves as the general method for the preparation of other RCo$_3$As$_2$ materials. We also show that the crystal structures and magnetic behavior of these arsenides are distinctly different from the properties of the corresponding phosphides.

**MATERIALS AND METHODS**

**Starting Materials.** Finely dispersed powders of lanthanum (99.9%) and neodymium (99.9%), as well as bismuth granules (99.99%), were obtained from Alfa Aesar and used as received. Cerium and neodymium filings were obtained from a metal chuck (Michigan Chemical Corporation, 99.9%) stored under oil, which was washed away with dry and air-free hexanes before filing. 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 drybox (content of O$_2$ < 1 ppm).

**Synthesis.** The starting materials were mixed in the R/Co/As/Bi = 1:2:2:30 ratio (total mass = 5 g; R = La, Ce, Pr, Nd) and loaded into 10 mm inner diameter (i.d.) fused silica tubes, which were sealed under vacuum (<10$^{-2}$ mbar). The mixtures were 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% aqueous H$_2$O$_2$ (1:1 v/v) for 2–3 days, followed by washings with dilute HCl (1:1 v/v) and water. The phase purity of samples with R = La, Ce, Pr was confirmed by powder X-ray diffraction, but the sample with R = Nd contained significant amount of impurities. The samples for neutron powder diffraction experiments were prepared by scaling up the total sample mass to 25 g (of which 23.5 g was Bi flux) and using larger silica tubes with 15 mm i.d. The scale-up also led to the formation of larger (~1 × 1 × 0.2 mm$^3$) single-crystals of RCo$_3$As$_2$, which were selected for magnetic property measurements.

**General Characterization Methods.** Powder X-ray diffraction was performed on a Rigaku DMAX 300 Ultima III powder X-ray diffractometer using Cu Kα 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 Kα$_1$, 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. Elemental analysis of selected 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 and single crystals with a Quantum Design SQUID magnetometer MPMS-XL. DC magnetic susceptibility measurements were carried out in an applied field of 1 mT in the temperature range 1.8–300 K. Isothermal field dependences of magnetization and hysteresis were measured with the magnetic field varying between −7 and +7 T.

**Single Crystal X-ray Diffraction.** For the room-temperature experiment, a single crystal was glued with epoxy cement on the tip of a quartz fiber and mounted on a goniometer head of a Bruker AXS SMART diffractometer equipped with an APEX-II CCD detector. The data sets were recorded as ω-scans in steps of 0.3° and integrated with the Bruker SAINT software. All the data sets were indexed in the tetragonal body-centered unit cell. The only systematic extinctions observed corresponded to the f-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 software. The structures were solved in the I4/mmm space group (No. 139), and the final refinement was performed with anisotropic atomic displacement parameters for Co and As atoms. The disorder Bi and R (R = La, Ce) 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 Table 1.

**Powder Neutron Diffraction.** Powder neutron diffraction experiments on R$_{1-x}$Bi$_x$Co$_3$As$_2$ (R = La, Ce) were carried out using the HB-2A high-resolution neutron powder diffractometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory. The $λ = 1.536 Å$ monochromatic radiation was provided by a vertically focusing Ge (115) monochromator. Measurements were carried out on a sample of ~3 g held in a cylindrical vanadium container placed in a top-loading closed cycle refrigerator, covering a temperature range 4–300 K. The data were collected by scanning the detector array consisting of 44 °He tubes in two segments, to cover the total 2θ range 7°–13° in steps of 0.05°. Overlapping detectors for the given step served to average the counting efficiency of each detector. More details about the HB-2A instrument and data collection strategies can be found in the original publication.

**Solid-State NMR Spectroscopy.** Field-sweep NMR and zero-field NMR measurements were performed in the 4.6–300 K range using a CPMAS probe equipped with a Bruker AM 400 spectrometer. Edges in the 13C MAS NMR spectrum were assigned to carboxylate groups.
Table 1. Data Collection and Structure Refinement Parameters for $R_x$ Bi$_y$ Co$_z$ As$_y$ ($R =$ La, Ce, Pr, Nd)

| compd. | La$_{0.97}$Bi$_{0.03}$Co$_{1.9}$As$_2$ | Ce$_{0.95}$Bi$_{0.05}$Co$_{1.85}$As$_2$ | PrCo$_{1.9}$As$_2$ | NdCo$_{1.75}$As$_2$
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"Further details of the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-422570 (La), 427525 (Ce), 427527 (Pr), and 427528 (Nd). Since the occupancy of the Co site was found to vary slightly from sample to sample, we will use the rounded values for the Co stoichiometry in the following discussion.

RESULTS AND DISCUSSION

Synthesis. In our numerous attempts to repeat the only literature report on the synthesis of RCo$_x$As$_y$ in Sn flux, we consistently arrived at samples contaminated by a large amount of byproducts. Thus, we concluded that alternative synthetic conditions were necessary to obtain phase-pure samples. As an alternative, we turned to reactions in molten Bi keeping in mind that this metal does not form any binary compounds with Co and As, and thus, the reaction might proceed in a different pathway as compared to the reaction in Sn flux. Indeed, the reaction between elements in Bi flux led to phase-pure samples of RCo$_x$As$_y$ (R = La, Ce, Pr) (Figure 1), although a negligible residual amount of elemental Bi also remains in the sample, as indicated by a very small X-ray diffraction peak at 20 ~ 28°.

When the reactions were scaled up, sufficient large plate-like single crystals were obtained, with approximate dimensions of 1 × 1 × 0.2 mm$^3$. The plane of the single crystal is perpendicular to the $c$ axis of the tetragonal structure, as indicated by the strong (00$l$) peaks in the X-ray powder diffraction pattern collected on a batch of oriented crystals (Supporting Information Figure S1). We could not obtain a phase-pure NdCo$_x$As$_y$ sample (Supporting Information Figure S2), but a

![Figure 1](image-url)
batch of single crystals was manually isolated to characterize the desired product. Attempts to prepare the analogous Sm- or Gd-containing compounds were unsuccessful, although the isostructural phosphide, SmCo$_2$P$_2$, is known.$^{ab}$

**Crystal Structure.** Single-crystal X-ray diffraction confirmed that all RCo$_2$As$_2$ phases crystallize in the ThCr$_2$Si$_2$ structure type, space group $I4/mmm$ (Figure 2). The EDX analysis revealed the average elemental ratio R/Co/As $\sim$ 1.2:1.8:2 (Table 2), which is close to the nominal 1:2:2 stoichiometry. The refinement of the crystal structure indicated the formation of $\sim$5–15% vacancies in the Co sublattice, which is in agreement with the slightly lower Co content detected by the EDX analysis. In addition, both La- and Ce-containing crystals showed significant residual electron density nearby the rare-earth crystallographic site (Wyckoff position 2a). The electron density peak was positioned at $\sim$0.5 Å away from the rare-earth site and could not be accounted for by the anisotropic atomic displacement of the R atom. Therefore, this site was assigned as partially occupied by Bi atoms, and the total occupancy of the R and Bi sites was constrained to 1. The incorporation of the extra atomic site into the structure of LaCo$_2$As$_2$ obtained from Bi flux is supported by the substantial increase of the unit cell parameter $c$ for this material as compared to the sample of LaCo$_2$As$_2$ prepared in the absence of Bi flux$^{12}$ (Table 2). It is puzzling, however, that the structure of CeCo$_2$As$_2$, which also reveals such dopant site, has nearly the same $c$ parameter when prepared with or without Bi flux. The $c$ parameter also remains nearly the same for both samples of PrCo$_2$As$_2$ or NdCo$_2$As$_2$, and no evidence for the Bi doping was observed in the structure of these compounds. The crystal structure refinement led to the final compositions La$_{0.97}$Bi$_{0.03}$Co$_{1.8}$As$_2$, Ce$_{0.95}$Bi$_{0.05}$Co$_{1.8}$As$_2$, Pr$_{0.95}$Co$_{1.8}$As$_2$, and Nd$_{0.97}$Co$_{1.8}$As$_2$. Noteworthy, a similar inclusion of Sn into the structure of BaFe$_2$As$_2$ was observed for the synthesis of this compound in Sn flux$^{25}$ while the formation of vacancies in the transition-metal sites was also found for other ThCr$_2$Si$_2$-type arsenides, for example, BaAg$_{0.97}$As$_2$, BaCu$_{1.95}$As$_2$, and CeNi$_{1.76}$As$_{0.24}$. We also note that the presence of a small amount (<2%) of Bi was conclusively established from the EDX microanalysis, but the accuracy of the determination is not sufficient to make a quantitative judgment about the Bi content against other elements present in the sample.

In the crystal structures of La$_{0.97}$Bi$_{0.03}$Co$_{1.8}$As$_2$ and Ce$_{0.95}$Bi$_{0.05}$Co$_{1.8}$As$_2$, the displacement of the Bi site relative to the more symmetric R site can be explained by the necessity to accommodate the stereoactive 6-fold lone pair of the Bi$^{3+}$ ion. This displacement results in a distorted coordination environment around Bi, with four longer and four shorter Bi–As bonds, as compared to the unique length of the eight R–As bonds (Table 3). The Bi inclusion, however, is not observed in the Pr- and Nd-containing structures, despite the presence of Co vacancies. This difference can be tentatively explained by the lanthanide contraction, which makes the lanthanide coordination cage less accommodating to the Bi$^{3+}$ ion (cf. lanthanide radii: Bi$^{3+}$, 1.17 Å; La$^{3+}$, 1.16 Å; Ce$^{3+}$, 1.14 Å; Pr$^{3+}$, 1.13 Å; Nd$^{3+}$, 1.11 Å). The substitution of Bi for lanthanides is not unprecedented; for example, it is well established for rare-earth ferrite garnets.$^{27}$

It is also noteworthy that the interlayer As–As distance in RCo$_2$As$_2$ changes quite consistently with the ionic radius of the R$^{3+}$ ions, from 2.880(2) Å for R = La to 2.721(5) Å for R = Nd (Table 3), in contrast to RCo$_2$P$_2$, where the interlayer P–P separation for R = La (3.162 Å) greatly exceeds the P–P distances for the other members of the series ($\sim$2.5–2.6 Å). Another structural difference can be gleaned from the

| Table 2. Results of EDX Analysis and Crystallographic Parameters of R$_{1-x}$Bi$_x$Co$_{2-y}$As$_2$ Determined by Room-Temperature Powder X-ray Diffraction$^a$ |
|------------------------|--------|------------|-------|--------|
| phase                 | EDX anal. | $a$, Å    | $c$, Å | $V$, Å$^3$ |
| La$_{0.97}$Co$_{1.8}$As$_2$ | 1.20(1):1.79(1):2 | 4.054 | 10.328 | 169.8 |
| La$_{0.97}$Bi$_{0.03}$Co$_{1.8}$As$_2$ | 1.20(1):1.79(1):2 | 4.0508(2) | 10.470(1) | 171.80(1) |
| LaCo$_2$P$_2$          | 3.815 | 11.041 | 160.6 |
| Ce$_{0.97}$Co$_{1.8}$As$_2$ | 1.19(3):1.76(4):2 | 4.026 | 10.216 | 165.6 |
| Ce$_{0.95}$Bi$_{0.05}$Co$_{1.8}$As$_2$ | 1.19(3):1.76(4):2 | 4.0238(8) | 10.217(2) | 165.81(1) |
| CeCo$_2$P$_2$          | 3.894 | 9.599 | 145.5 |
| Pr$_{0.95}$Co$_{1.8}$As$_2$ | 1.19(9):1.8(1):2 | 4.017 | 10.169 | 164.1 |
| Pr$_{0.95}$Bi$_{0.05}$Co$_{1.8}$As$_2$ | 1.19(9):1.8(1):2 | 4.0211(5) | 10.167(1) | 164.40(1) |
| PrCo$_2$P$_2$          | 3.900 | 9.759 | 148.4 |
| Nd$_{0.97}$Co$_{1.8}$As$_2$ | 1.15(3):1.61(4):2 | 4.006 | 10.078 | 161.7 |
| Nd$_{0.97}$Bi$_{0.03}$Co$_{1.8}$As$_2$ | 1.15(3):1.61(4):2 | 4.014(4) | 10.09(1) | 162.53(2) |
| NdCo$_2$P$_2$          | 3.891 | 9.687 | 146.7 |

$^a$A comparison to the parameters of RCo$_2$P$_2$ is also provided. $^b$The R/Co/As atomic ratio. The amount of Bi in the La- and Ce-containing samples could not be established from the EDX analysis due to the low content of this element.
comparison of the Co–Co distances. In RCo₅P₂, the decrease in the interlayer P–P distance resulted in a significant increase in the intralayer Co–Co distance, but in RCo₂As₂ both As–As and Co–Co distances decrease with the lanthanide contraction (Table 3). Similar to the shorter P–P distances in RCo₅P₂, the As–As distances in RCo₂As₂ notably exceed the typical length of the As–As single bond (2.43 Å), suggesting the absence of any significant As–As bonding in these structures. Thus, the interlayer cohesion between the [Co₂As₄] slabs is mainly provided by the R–As bonding.

**XANES Spectroscopy.** Based on the analysis of magnetic properties and unit cell volumes of the RCo₅P₂ series, Jeitschko et al. deduced that Ce atoms exhibit valence fluctuations in CeCo₅P₂. These earlier findings incited us to examine the oxidation state of Ce in Ce₀.₃₅Bi₀.₆₅O₁.₈₅As₂ by means of XANES spectroscopy at the L₃ edge of Ce. A spectrum obtained at room temperature is shown in Figure 3. It can be deconvoluted into two contributions corresponding to Ce³⁺ and Ce⁴⁺ oxidation states. The former component clearly dominates the spectrum. Therefore, Ce₀.₃₅Bi₀.₆₅O₁.₈₅As₂ can be classified as a slightly mixed-valent compound with the average oxidation state of Ce equal to +3.06, which remains essentially the same from 10 to 300 K (Supporting Information Figure S3, Table S1). The XANES measurements also confirmed that the oxidation states of La in La₀.₇Bi₀.₃Co₁.₉As₂ and Pr in PrCo₁.₉As₂ are equal to +3 (Supporting Information Figure S4).

**Magnetic Properties.** La₀.₉Bi₀.₁Co₁.₉As₂. Magnetic measurements on a polycrystalline sample of La₀.₉Bi₀.₁Co₁.₉As₂ revealed that this compound exhibits FM ordering at Tₐf = 178 K (Figure 4), where the Tₐf value was determined from the minimum of the dχ/dT derivative curve. A negligible coercivity observed in the hysteresis loop measured at 1.8 K indicates that La₀.₉Bi₀.₁Co₁.₉As₂ is a soft ferromagnet (Supporting Information Figure S5). Nevertheless, the divergence of the zero-field-cooled (ZFC) and field-cooled (FC) susceptibility curves suggests some magnetic anisotropy in the Co sublattice.

To further investigate the magnetic anisotropy of La₀.₉Bi₀.₁Co₁.₉As₂, magnetic measurements were performed on an oriented single crystal of this compound. The magnetic field (H = 1 mT) was applied parallel and perpendicular to the tetragonal c axis, revealing a strong preference of the Co moments to be magnetized along the c axis (Figure 5a). With H||c, the magnetization is saturated already at ~0.1 T, while with H⊥c, the saturation is reached only at ~6.5 T (Figure 5b). Based on the field-dependent magnetization data collected at 1.8 K, the saturation magnetization value is 0.59(1) μₐB per Co atom. Interestingly, the preferred alignment of Co moments in La₀.₉Bi₀.₁Co₁.₉As₂ differs dramatically from that found in the magnetic structure of LaCo₅P₂, where the Co moments exhibit FM alignment parallel to the ab plane.²⁹

![Figure 3. L₃-Ce XANES spectrum of Ce₀.₃₅Bi₀.₆₅O₁.₈₅As₂ at room temperature.](image)

![Figure 4. Temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities of a polycrystalline sample of La₀.₉Bi₀.₁Co₁.₉As₂ measured under magnetic field of 1 mT.](image)

Table 3. Interatomic Distances (Å) in the R₁₋ₓBiₓCo₂₋ₙAs₂ Structures As Determined by Single-Crystal X-ray Diffraction Analysis at 298 K

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<td>PrCo₁.₉As₂</td>
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<td>3.2247(7)</td>
<td>2.7215(6)</td>
<td>2.8329(8)</td>
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![Image](image)
exhibits fast increase in magnetization at 75 K due to the ordered Co moments followed by the gradual linear increase due to the paramagnetic disordered Ce moments. The magnetization curve obtained at 25 K is nearly the same, with the slightly larger initial increase, as can be expected from the better alignment of the FM ordered Co domains due to the lower thermal energy. The field-dependent magnetization collected at 1.8 K, however, shows a substantial coercivity that must be emerging from the ordering of Ce magnetic moments with high magnetocrystalline anisotropy.

The magnetic anisotropy of Co and Ce sublattices can be observed in the single-crystal magnetic measurements. Similar to La_{0.97}Bi_{0.03}Co_{1.9}As_2, the magnetic moments show a strong preference to ordering along the c axis (Figure 7a). Besides the sharp rise below $T_C = 147$ K due to the ordering of $3d$ moments, another feature is observed in the susceptibility curve around 70 K. This anomaly is probably associated with the gradual ordering of $4f$ moments. The hysteresis loop measured at 1.8 K with $H \parallel c$ (Figure 7b) exhibits large coercivity (0.6 T) and remanence (1.2 $\mu_B$) associated with the high magnetocrystalline anisotropy of the Ce sublattice. With $H \perp c$, the
coercivity becomes even larger (1 T) but the saturation magnetization is substantially lower and the remnant magnetization drops nearly to zero when the magnetic field is removed. At this point, we need to consider the possible nature of magnetic exchange between the 3d moments of Co and the 4f moments of Ce. In the case of related RCo$_x$ intermetallics, it was established that the 3d-4f exchange is always FM for the lighter rare-earth ions, with less than half-filled 4f subshell. The theoretically expected magnetization of the Ce$^{3+}$ ion is equal to 2.14 $\mu_B$ or, when corrected for the oxidation state of Ce (+3.06) found from XANES spectra, 2.01 $\mu_B$ in Ce$_{0.05}$Bi$_{0.03}$Co$_{1.85}$As$_2$. The magnetic moment per Co atom can be approximated as 0.59 $\mu_B$ from the magnetic properties of La$_{0.75}$Bi$_{0.05}$Co$_{1.8}$As$_2$ (Figure 5b), which is also close to the value found from the initial increase in the magnetization of Ce$_{0.05}$Bi$_{0.03}$Co$_{1.85}$As$_2$ at 25 K (Figure 6b). Hence, if the Ce and Co moments were parallel to each other, the total expected saturation magnetization would be equal to $\sim 3.09 \mu_B$, taking into account the composition of the compound. This is much higher than the actual saturation value of 1.33 $\mu_B$ observed at 1.8 K. On the other hand, if we assume AFM 3d-4f exchange, the expected saturation magnetization should be $\sim 0.73 \mu_B$, which is closer to the value observed, but still somewhat lower. This analysis of magnetization data suggests noncollinear AFM coupling between the Ce and Co magnetic moments in Ce$_{0.05}$Bi$_{0.03}$Co$_{1.85}$As$_2$. This hypothesis is also in agreement with our recent finding of FM ordering in La$_{0.75}$Pr$_{0.25}$Co$_{2}$P$_2$. We also note that the magnetic behavior of Ce$_{0.05}$Bi$_{0.03}$Co$_{1.85}$As$_2$ is strikingly different from that of CeCo$_2$P$_2$ which exhibits AFM ordering in both Ce and Co sublattices. Later, in the neutron diffraction section, we will return to the discussion of the magnetic ordering in Ce$_{0.05}$Bi$_{0.03}$Co$_{1.85}$As$_2$.

PrCo$_{1.8}$As$_2$. Similar to the La- and Ce-containing analogues, PrCo$_{1.8}$As$_2$ exhibits FM ordering of Co moments at $T_C = 140$ K, as shown by the ZFC and FC susceptibility measurements on a polycrystalline sample (Figure 8). This behavior is strikingly different from the isostructural phosphide, PrCo$_2$P$_2$, where the Co moments show AFM ordering at $T_N = 309$ K. In the low-temperature regime, a significant decrease in the magnetic moment is observed below 50 K. Such magnetic behavior of PrCo$_{1.8}$As$_2$ is similar to the behavior of La$_{0.75}$Pr$_{0.25}$Co$_2$P$_2$, suggesting AFM coupling between the 3d and 4f magnetic moments. The temperature-dependent FC susceptibility curve is typical of a ferrimagnet with different anisotropies of two magnetic sublattices. As the temperature is decreased below $T_C$, the soft Co moments order first, causing the abrupt increase in the magnetization, while the hard Pr moments order gradually under the influence of the internal magnetic field induced by the Co moments, resulting in the decrease in the total magnetization value. At $T_{comp} = 9$ K, the contributions from both sublattices become nearly equal, which leads to the observation of zero magnetization at this temperature and negative magnetization values below 9 K, a phenomenon known as the magnetic pole reversal.

The anisotropy of magnetic properties is observed in the magnetic measurements on a single crystal of PrCo$_{1.8}$As$_2$. Similar to La$_{0.75}$Bi$_{0.05}$Co$_{1.8}$As$_2$ and Ce$_{0.05}$Bi$_{0.03}$Co$_{1.85}$As$_2$, the magnetic moments prefer to order along the c axis (Figure 9a). The field-dependent magnetization measured with $H||c$ at 100 K exhibits an abrupt increase, confirming the FM ordering in the magnetically soft Co sublattice (Figure 9b), while with $H\perp c$ the magnetization increases slowly, as expected for the direction perpendicular to the easy axis (Supporting Information Figure S6a). A gradual linear increase in the $H||c$ magnetization is observed as the field increases, which confirms the paramagnetism of the Pr sublattice at 100 K. At 30 K, this linear increase becomes much more pronounced, in agreement with the purport of gradual ordering of the Pr moments under the influence of the FM ordered Co sublattice. The magnetic moment per Co atom estimated from the initial ordering of Co moments at 30 K equals to 0.37 $\mu_B$. The magnetization behavior at 1.8 K is very different. Instead of the fast initial rise, we observe a gradual linear increase to a plateau of 1.4 $\mu_B$ followed by a metamagnetic transition at $H_{c1} = 4.2$ T and saturation of the total magnetization at 3.0 $\mu_B$. This value is slightly lower than the theoretical expectation for the Pr$^{3+}$ ion (3.2 $\mu_B$) and thus suggests a noncollinear AFM coupling between the Pr and Co moments, similar to the situation observed in Ce$_{0.05}$Bi$_{0.03}$Co$_{1.85}$As$_2$. The magnetization behavior measured on a polycrystalline sample of PrCo$_{1.8}$As$_2$ at 1.8 and 100 K (Supporting Information Figure S6b) is very similar to that observed for the single-crystal sample with $H||c$.

It appears, however, that the noncollinear FM state in PrCo$_{1.8}$As$_2$ is only stabilized at high fields, because the metamagnetic behavior at lower fields suggests the initial presence of an AFM state. We also note a small feature around 7 K in the temperature-dependent FC magnetization curve at $H||c$ (Figure 9a), which indicates a possible second (AFM) magnetic phase transition in PrCo$_{1.8}$As$_2$. Indeed, an examination of a hysteresis curve recorded for the single crystal of PrCo$_{1.8}$As$_2$ at 1.8 K (Figure 10) reveals two metamagnetic transitions, with the critical fields of 1.3 and 4.4 T. As the field is increased in either positive or negative direction, the initial small increase of magnetization to $\sim 0.5 \mu_B$ is followed by the first metamagnetic step to 1.3 $\mu_B$ and then by the second metamagnetic step to 2.9 $\mu_B$. Taking into account the possible magnitudes of the Co 3d and Pr 4f magnetic moments discussed above, the stepwise growth of magnetization appears to correspond to the FM magnetization of Co moments, followed by switching of a half of Pr moments from the AFM to FM order at $\sim 1.5$ T, and finally by switching of the other half of Pr moments from the AFM to FM order at $\sim 4.5$ T. In both metamagnetic transitions, the reoriented Pr 4f moments become coupled AFM to the Co 3d moments. Such sequence

![Figure 8](dx.doi.org/10.1021/cm501522v) | Chem. Mater. 2014, 26, 3825–3837
of field-dependent magnetic phase transitions is also in agreement with the larger increase in the total moment at the second step as compared to the increase at the first step. Nevertheless, it is not clear why the Pr moment should reorient in such a stepwise manner. At the very least, these observations suggest the structure of the magnetically ordered ground state might be more complicated than just simple alignment of moments parallel to the c axis. Further studies, including neutron diffraction, X-ray magnetic circular dichroism spectroscopy, and magnetoresistance measurements, will be undertaken to verify the proposed scenario and establish the field-dependent magnetic structures.

NdCo$_{1.7}$As$_2$. We were not able to obtain a phase-pure sample of NdCo$_{1.7}$As$_2$, and the crystals of this compound were too small for single-crystal magnetic measurements. Therefore, the measurements were performed only on a batch of several manually selected crystals. The magnetic behavior of NdCo$_{1.7}$As$_2$ is similar to that of PrCo$_{1.8}$As$_2$. The FM ordering of Co moments at $T_C = 62$ K is followed by an abrupt decrease in the FC susceptibility nearly to zero at lower temperatures (Figure 11a), in agreement with AFM $3d$-$4f$ exchange. Another turning point in the $\chi$ vs $T$ curve is observed at 6 K. The field-dependent magnetization at 1.8 K also reveals two metamagnetic transitions (Figure 11b). The first critical field is $\sim 3.5$ T while only an onset of the second field-induced event is observed at 7 T, with the maximum saturation value of 1.66 $\mu_B$ reached at this field. Since the expected saturation magnetization per Nd$^{3+}$ ion is 3.28 $\mu_B$, it appears that, similar to PrCo$_{1.8}$As$_2$, the two metamagnetic transitions correspond to the stepwise reorientation of the Nd magnetic moments to afford the FiM ground state.

Neutron Powder Diffraction. Jeitschko et al. established the magnetic structures of the isostructural compounds RCo$_2$P$_2$.
Figure 12. NMR spectra of La_{0.97}Bi_{0.03}Co_{1.9}As_{2} measured at 44.1 MHz for different temperatures. The positions of the free Larmor precessions of all nuclei under investigation are shown by short vertical lines. Extrinsic signals $^{3}H$, $^{19}F$, and $^{65,63}Cu$ are due to the experimental set-up.

by neutron diffraction studies. We also turned to this method to probe the magnetic structures of La$_{0.9}$Bi$_{0.03}$Co$_{1.9}$As$_{2}$ and Ce$_{0.95}$Bi$_{0.05}$Co$_{1.85}$As$_{2}$. (We could not perform such studies on PrCo$_{1.8}$As$_{2}$ because attempts to scale up the preparation did not afford sufficiently pure samples.) The diffraction data were collected above and below the magnetic ordering temperatures but did not reveal any magnetic peaks below $T_{C}$. Rietveld refinement of the nuclear structure of both compounds resulted in the unit cell parameters $a = 4.0592(1)$ Å, $c = 10.4830(5)$ Å for $R = La$ and $a = 4.0396(2)$ Å, $c = 10.2202(5)$ Å for $R = Ce$, in agreement with the values refined from the room-temperature powder X-ray diffraction data (Table 2). The structural refinements led to formulas LaCo$_{1.73}$As$_{2}$ and CeCo$_{1.8}$As$_{2}$, respectively (Supporting Information Figures S7 and S8, Table S2), which confirm the presence of Co vacancies established from the single-crystal X-ray diffraction data. The occupancy of the possible Bi site was not refined, due to the very similar scattering lengths of Bi (8.532 fm) and La (8.24 fm) and the low amount of Bi present in the structures. Nevertheless, we note yet again the significantly larger $c$ parameter of the La-containing samples obtained from Bi flux (10.470(1) Å from X-ray and 10.4830(5) Å from neutron powder diffraction) as compared to the $c$ parameter reported for the sample obtained by a solid-state reaction between the elements (10.328 Å). One shall note that the FM ordering of Co moments along the $c$ axis is expected to produce magnetic scattering at the (110) reflection, which contains a significant nuclear scattering contribution. This is in contrast to the neutron diffraction patterns of FM LaCo$_{2}P_{2}$ and La$_{0.5}$Pr$_{0.5}$Co$_{2}P_{2}$, where the presence of a weak magnetic (002) reflection is caused by the FM ordering of Co moments in the $ab$ plane. The relatively large structure factor associated with the nuclear component of the (110) reflection in RCo$_{2}$As$_{2}$ (Supporting Information Figure S9) introduces a strong limitation on the magnitude of the FM moment that can be detected by using unpolarized neutrons. Indeed, our simulation of the neutron powder diffraction patterns of LaCo$_{1.73}$As$_{2}$ and CeCo$_{1.8}$As$_{2}$ for the experimentally determined FM ordering of 3$d$ moments along the $c$ axis ($\sim 0.6 \mu_B$ per Co atom) demonstrates that the contribution of this magnetic structure to the pattern is negligible (Supporting Information Figure S10). On the other hand, if one assumed antiparallel alignment of 3$d$ and 4$f$ moments at lower temperatures, with the calculated moment of $\sim 2.0 \mu_B$ per Ce atom, both (110) and (101) reflections should have been strongly enhanced, but we do not observe such enhancement experimentally. Neither can we reject magnetic ordering in the Ce sublattice, given the large magnetic hysteresis found for Ce$_{0.95}$Bi$_{0.05}$Co$_{1.85}$As$_{2}$ in contrast to the magnetic softness of La$_{0.97}$Bi$_{0.03}$Co$_{1.9}$As$_{2}$. All these considerations lead us to believe that the lowest-temperature magnetic structure of Ce$_{0.95}$Bi$_{0.05}$Co$_{1.85}$As$_{2}$ involves, at the very least, noncollinear AFM arrangement between the Ce and Co moments, if not an even more complicated magnetic ordering. Polarized neutron diffraction experiments able to provide increased sensitivity to the FM ordering along the $c$ axis in both R and Co sublattices are planned for the future.

**Solid-State NMR Spectroscopy.** NMR spectroscopy experiments were carried out on a polycrystalline sample of La$_{0.97}$Bi$_{0.03}$Co$_{1.9}$As$_{2}$. There are three NMR active nuclei in this material: $^{95}$Co, $^{75}$As, and $^{139}$La. In addition to these intrinsic isotopes, we observed extrinsic NMR signals which were...
introduced due to the experimental set up, that is, $^3$H from paraffin, $^{19}$F from the Teflon sample holder, and $^{63,65}$Cu from the copper coil of the tank circuit. Field-sweep NMR spectra measured at a fixed frequency of 44.1 MHz for different temperatures are shown in Figure 12. As the temperature is lowered, the spectra become more complex, and the one at 4.5 K demonstrates a complicated shape with several broad lines in the entire magnetic field range available (0–9.4 T). In order to assign these lines properly, we measured isothermal field-sweep NMR spectra at 4.7 K at various fixed frequencies (Figure 13a). The field positions of characteristic resonance lines are labeled A–E in Figures 12 and 13a and are plotted as a function of frequency in Figure 13b, following the approach developed by us earlier.\(^\text{13}\) In this figure, we also plot solid lines that give the linear relation $H(\nu) = (\nu/2\pi)^{-1} \gamma_T$, according to the free Larmor precessions of the $^{59}$Co ($\nu/2\pi = 10.05$ MHz/T), $^{75}$As ($\nu/2\pi = 7.29$ MHz/T), and $^{139}$La ($\nu/2\pi = 5.62$ MHz/T) nuclei.

An analysis of the frequency dependence of resonance fields reveals that lines B and D belong to minor impurity phases. Thus, one can easily assign the intensive and narrow line B to $^{59}$Co nuclei in the diamagnetic cubic impurity phase (exactly observed at the position of the free Larmor precession, $\nu/2\pi = 10.05$ MHz/T, without any shift or quadrupole splitting). The very small line D originates from $^{139}$La nuclei of some La-containing impurity. The corresponding linear dependences are shown in Figure 13b with dashed red (B, $^{59}$Co) and magenta (D, $^{139}$La) lines. The minor impurity might be the cubic LaCoO$_3$ phase, but its amount was below the detection limit of powder X-ray diffraction.

The other three lines, A, C, and E, can be assigned to the major phase, La$_{0.97}$Bi$_{0.03}$Co$_{1.9}$As$_2$, as their positions and intensities change significantly as the temperature is increased above the Curie point, $T_C = 178$ K. Thus, the high-field line E shifts to lower fields, toward the $^{139}$La Larmor field value, with increasing temperatures above 150 K (cf. Figure 12). The best fit of the $H$ vs $\nu$ data for this signal is shown with the solid black line (Figure 13b), which gives the linear coefficient of 0.175(4) T/MHz, close to $(139\nu/2\pi)^{-1} = 0.166$ T/MHz. From the intercept of this linear fit with the resonance field axis (black circle) one obtains the value of the hyperfine field at the La site in La$_{0.97}$Bi$_{0.03}$Co$_{1.9}$As$_2$ to be $H_{hf}(La) = 2.61(1)$ T.

The broad line C also shifts to lower fields, toward the $^{59}$Co Larmor field value, with increasing temperature and merges with the $^{59}$Co line B from the impurity phase for $T > 170$ K (Figure 12), resulting in the solitary, asymmetric line observed at the $^{59}$Co Larmor field for 210 K. Such temperature behavior of the chemical shift unambiguously proves that the line C originates from $^{59}$Co nuclei. Therefore, the $H$ vs $\nu$ data for this signal were fitted to the linear function, $H = a + b(\nu/2\pi)\nu = 0.0995$ T/MHz. The best-fit constant term $b$ gives the value of the hyperfine field at the Co site in La$_{0.97}$Bi$_{0.03}$Co$_{1.9}$As$_2$ to be $b = H_{hf}(Co) = 1.3(1)$ T. This value of the hyperfine field $H_{hf}$ is very small, in comparison to that at the La site. Probably, this line represents not all Co atoms but only those nearest to the Bi defects at the La sites, where the hyperfine field is strongly reduced due to the high diamagnetism of the Bi atoms. This assumption is strongly corroborated by the fact that our $^{59}$Co spectral lines in La$_{0.97}$Bi$_{0.03}$Co$_{1.9}$As$_2$ exhibit no splitting in central and satellite contributions due to the interaction of the nuclear electric quadrupole moment with the surrounding electrical field gradient (EFG). In general, the ThCr$_2$Si$_2$-type structures exhibit an appreciable EFG with axial symmetry along the crystallographic c-axis at the transition metal site,\(^\text{54}\) but a distortion of the local EFG due to Bi defects at the La sites yields a collapse of the spectral pattern with distinct central and satellite contributions into one, solitary broad single line, as we observe for the Co site.

To validate this assignment and for better understanding of the low-temperature magnetic structure of La$_{0.97}$Bi$_{0.03}$Co$_{1.9}$As$_2$, we performed zero-field NMR measurements at 15 K sweeping the irradiation frequency, $\nu$, step-by-step. Although the spectrum is rather broad and complicated, it contains two distinct lines (Figure 14). The left narrow peak corresponds to the $^{139}$La zero-field NMR signal originating from the non-disturbed by Bi defects La sites with nearly zero electric field

![Figure 13.](image-url)
gradient (EFG). Taking into account the Larmor precession of the $^{139}$La nucleus ($\gamma/2\pi = 5.62 \text{ MHz/T}$), the position of this peak provides an estimate of the local field at the La site to be 2.59(2) T. This value is in very good agreement with the value of the hyperfine field $H_{hf}(\text{La})$ estimated from the line E in the $H$ vs $\nu$ diagram (shown as black circle in Figure 13b).

Finally, the position of the broad NMR peak at $\sim43.2$ MHz (Figure 14) coincides well with the low-field line A in the $H$ vs $\nu$ diagram (Figure 13b, cyan circle). This line shows an opposite frequency dependence with the absolute value of the linear coefficient equal to 0.139(6) $\text{ T/MHz}$, which is in perfect agreement with the value of inverse Larmor precession expected for $^{75}$As: $(\gamma/2\pi)^{-1} = 0.137 \text{ T/MHz}$. From the peak frequency of 43.2(1) MHz one estimates the value of the hyperfine field to be $H_{hf}(\text{As}) = 5.92$ T.

Actually, in the zero-field NMR spectrum the spin–echo intensity was observed in the entire frequency range 13–65 MHz (Figure 14). This might be due to the wide distribution of local magnetic fields and EFGs on the Co and As sites in the vicinity of Bi defects. Overall, we observed very complicated field-sweep NMR spectra and the broad zero-field NMR spectrum for La$_{0.5}$Bi$_{0.5}$Co$_{1.5}$As$_2$ at low temperatures. The values of the local magnetic fields of 2.59(2) T and 5.92(1) T on $^{139}$La and $^{75}$As nuclei, respectively, were determined in the magnetically ordered state. A strong reduction of the local magnetic field on $^{99}$Co nuclei in the vicinity of Bi defects was observed.

Electronic Structure. Nonpolarized electronic band structures of LaCo$_2$As$_2$ and PrCo$_2$As$_2$ were calculated using the LMTO approach to elucidate the origin of magnetic ordering. The calculations were performed on idealized crystal structures, without inclusion of Bi defect sites or Co vacancies. The nonmagnetic calculations revealed a very strong peak in the density of states (DOS) at the Fermi level, mainly arising from the contribution of the Co 3d orbitals (Figure 15, top). Approximating the Co–Co exchange interaction ($J$) by the value reported for the free Co metal, $^{35}$ we find that the value of DOS at the Fermi level, $n(E_F)$, allows the satisfaction of the Stoner criterion for itinerant ferromagnetism, $Jn(E_F) > 1$. $^{36}$ The results of DFT calculations lead to $Jn(E_F) = 2.1$ for LaCo$_2$As$_2$ and PrCo$_2$As$_2$, respectively. A criterion proposed by Dronskowski suggests the need for strong antibonding interactions at the Fermi level as the driving force for the FM ordering. $^{37}$ Indeed, the crystals orbital Hamilton population (COHP) analysis of the Co–Co bonding in LaCo$_2$As$_2$ and PrCo$_2$As$_2$ reveals the strong antibonding character of Co–Co interactions in the [Co$_2$As$_2$] layer (Figure 15, bottom), thus satisfying the Dronskowski’s criterion and supporting the FM ordering observed experimentally.

The spin-polarized band structure calculations were performed on the idealized structures of LaCo$_2$As$_2$ and PrCo$_2$As$_2$ using the FPLO code. The strong polarization of the Co 3d subband (Figure 16) is consistent with the itinerant FM ordering. The calculations resulted in the expected magnetic moment of 0.75 $\mu_B$ per Co atom in on LaCo$_2$As$_2$, which is in reasonable agreement with the measured value of 0.59 $\mu_B$ at 1.8 K. For PrCo$_2$As$_2$, the calculation was based on a FM ground state model in which the Pr and Co moments were set antiparallel to each other. The calculated magnetic moment of Pr (2.1 $\mu_B$) was lower than the theoretically expected value (3.2 $\mu_B$), while the calculated Co moment (0.75 $\mu_B$) was higher than the value obtained from the field-dependent magnetization at 30 K (0.37 $\mu_B$). This discrepancy suggests that our calculations might have certain shortcomings, especially with regard to the treatment of 4f magnetism for the Pr$^{3+}$ ions with the strong spin–orbit coupling, as well as that the real magnetic structure might be more complicated than the simple FM model. One also should keep in mind that the calculations were performed for the idealized structures of LaCo$_2$As$_2$ and PrCo$_2$As$_2$, but the presence of Co vacancies, undoubtedly, influences the crystal orbital populations and the spin polarization at $E_F$.

### CONCLUDING REMARKS

This work establishes Bi flux as an effective reaction medium for the synthesis of ternary arsenides, RCo$_2$As$_2$ ($R = \text{La–Nd}$). The X-ray crystal structure determination reveals the formation of Co vacancies in all these materials, as well as the incorporation of Bi defects into the structures of La- and Ce-containing phases, leading to the general formula...
The formation of Co vacancies was also confirmed by EDX microanalysis and Rietveld structural refinement from neutron powder diffraction data. All compounds exhibit ferromagnetic (FM) ordering of Co magnetic moments at higher temperature. Magnetic studies on single crystals show that the Co moments align along the tetragonal c axis. At lower temperatures, the rare-earth magnetic moments (for R = Ce, Pr, Nd) order antiparallel to the Co moments, stabilizing a ferrimagnetic (FiM) ground state. The NMR spectroscopy performed on La_{0.97}Bi_{0.03}Co_{1.8}As_2 provides the values of the local magnetic fields of 2.59(2) T and 5.92(1) T on the ^{139}La and ^{75}As nuclei, respectively, in the magnetically ordered state. We also observed a strong reduction of the local magnetic field on the ^{99}Co nuclei in the vicinity of Bi defects. Interestingly, the Pr- and Nd-containing samples are likely antiferromagnetic (AFM) at the lowest temperature of our experiments, as the magnetization measurements at 1.8 K revealed two consecutive metamagnetic transitions. Further studies, employing polarized neutron diffraction and X-ray magnetic circular dichroism spectroscopy, will be performed in the future to shed light on the field-dependence and magnetically ordered structures of Ce_{0.97}Bi_{0.03}Co_{1.8}As_2, PrCo_{1.8}As_2, and NdCo_{1.8}As_2.

We note that the magnetic behavior of RCo_{2}As_2 is quite different from that established for the isostructural phosphides, RCo_{2}P_2. All the RCo_{2}As_2 materials exhibit FM ordering of Co 3d moments along the c axis, while among the corresponding phosphides only LaCo_{2}P_2 shows FM ordering of Co moments, which are aligned parallel to the ab plane. All the other RCo_{2}P_2 phases exhibit AFM ordering in the Co sublattice near or above the room temperature and AFM ordering in the R sublattice below 20 K. Thus, the 3d and 4f magnetic orderings are “decoupled” in RCo_{2}P_2 because of the cancellation of Co moments at rather high temperatures. In contrast, the FM ordering of Co moments in RCo_{2}As_2 allows the observation of the 3d-4f coupling effects in these materials. Especially interesting is the fact that this 3d-4f exchange is AFM in nature, resulting in FiM ground states for R = Ce, Pr, and Nd. This situation is in drastic contrast to the well-established properties of related layered binary structures, RCo_{2}, in which the 3d and 4f moments are always coupled FM for the lighter lanthanides. Therefore, our findings indicate that the nonmetal atoms should play a significant role in defining the character of magnetic exchange interactions in RCo_{2}As_2. Undoubtedly, further experimental and theoretical studies are required to better understand the nature and mechanisms of the magnetic phase transitions observed in these materials.

**REFERENCES**


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