

Filling the holes in the CaFe_4As_3 structure: Synthesis and magnetism of CaCo_5As_3

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Here, we investigate single crystals of CaCo_5As_3 by means of single-crystal x-ray diffraction, microprobe, magnetic susceptibility, heat capacity, and pressure-dependent transport measurements. CaCo_5As_3 shares the same structure of CaFe_4As_3 with an additional Co atom filling a lattice vacancy and undergoes a magnetic transition at $T_M = 16$ K associated with a frustrated magnetic order. CaCo_5As_3 displays metallic behavior and its Sommerfeld coefficient ($\gamma = 70$ mJ/mol K²) indicates a moderate enhancement of electron-electron correlations. Transport data under pressures to 2.5 GPa reveal a suppression of T_M at a rate of -0.008 K/GPa. First-principles electronic structure calculations show a complex three-dimensional band structure and magnetic moments that depend on the local environment at each Co site. Our results are compared with previous data on CaFe_4As_3 and provide a scenario for a magnetically frustrated ground state in this family of compounds.

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I. INTRODUCTION

Transition-metal pnictides and chalcogenides have attracted renewed interest in the past decade. From the discovery of high-temperature superconductivity in the Fe-based superconductors [1,2] to the experimental realization of a Weyl semimetal state in TaAs [3–5], these materials have become a promising avenue for the investigation of new states of matter. Although distinct phenomena emerge in different families of transition-metal pnictide compounds, a strong correlation between crystal structure and physical properties is commonplace. In the case of TaAs, spin-orbit coupling and inversion symmetry breaking are key to realizing a Weyl semimetal state. In the case of FeAs-based superconductors, the layered tetragonal structure containing planes of FeAs₄ tetrahedra is present in all superconducting families.

The search for new materials not only furthers understanding of the relationship between structure and materials' properties but also can lead to the discovery of new states that emerge from novel structural arrangements. For instance, CaFe_4As_3 was synthesized soon after the report of superconductivity in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ at $T_c = 38$ K [6,7]. CaFe_4As_3 crystallizes in an orthorhombic structure with interpenetrating FeAs strips that also contain FeAs₄ tetrahedra. As shown in Fig. 1(a), these strips have a finite width in the ac plane and are connected through fivefold coordinated Fe atoms [Fe(4)], creating channels that host Ca atoms. Thermodynamic measurements on CaFe_4As_3 (“143”) single crystals reveal a second-order transition at $T_N = 89.6$ K. Neutron diffraction measurements find that the transition at T_N is to a longitudinal ($\parallel b$) incommensurate (IC) spin-density-wave (SDW) order with a three-dimensional (3D) Heisenberg-like critical exponent [8]. At $T_2 = 25.6$ K, there is a first-order transition to a commensurate order due to the loss of a degree of freedom associated with a soft mode present in the IC state. Band-structure calculations in the nonmagnetic regime appear to be consistent with a nesting instability associated with the planar Fermi sheets from cross-linked FeAs strips [8]. Subsequent first-principles calculations, however, note that the nesting concept would be only valid in the linear perturbation regime over the calculated nonmagnetic state, and, as a consequence, inapplicable for a strongly magnetic state. In fact, the ordered moments extracted from neutron diffraction

below T_2 are $2.2\mu_B$ and $2.4\mu_B$ per Fe²⁺ (fourfold) and Fe⁺ (fivefold) sites, respectively. These values are considerably larger than those in Fe-based superconductors ($0.4\text{--}1\mu_B/\text{Fe}$), but comparable to the moment of strongly correlated FeTe ($2.1\mu_B$) [9]. Moreover, the magnetic structure realized in CaFe_4As_3 is similar to that of $\text{Fe}_{1.14}\text{Te}$ [10].

Theoretical and experimental reports on the Fe Pn -based materials ($Pn = \text{pnictogen, chalcogen}$) show that the Fe moment is sensitive to the Fe- Pn hybridization and tends to increase with increasing Fe- Pn distance [9,11,12]. In fact, the Fe-Te distance in $\text{Fe}_{1.14}\text{Te}$ (2.59 Å) is comparable to the Fe-As distances in CaFe_4As_3 (2.4–2.61 Å) but significantly larger than corresponding distances in the small-moment parent compounds CaFe_2As_2 (2.37 Å) and BaFe_2As_2 (2.39 Å). Density functional calculations suggest that thicker Fe Pn planes stabilize magnetic structures found in FeTe and CaFe_4As_3 due to the effect of bond angles on second- and third-nearest-neighbor interactions [13]. Further, as noted in Ref. [8], the sequence of phase transitions observed in CaFe_4As_3 also occurs in TbMnO_3 [14] and $\text{Ni}_3\text{V}_2\text{O}_8$ [15], and can be explained by a combination of competing exchange interactions and easy-axis anisotropy. Finally, the simplest of the FeAs-based compounds, FeAs, is highly orthorhombic and also orders in an IC-SDW. First-principles calculations on FeAs show that there is no correspondence whatsoever between the computed real part of the susceptibility and the ordering vector [16]. This result indicates that the common ordering pattern is not nesting driven in these materials. In particular, next-nearest neighbors in FeAs have parallel spins and the Fe-As-Fe bond angle is close to 90° whereas nearest neighbors have opposite spins and much flatter angles, consistent with the Goodenough-Kanamari rules. Though these rules were derived for dielectrics, the observed agreement hints to the presence of local-moment physics.

All of the above suggests a scenario in which magnetic frustration plays a role and IC-SDW order in CaFe_4As_3 arises from competing magnetic couplings. Geometrical frustration in metals and insulators has been explored extensively in pyrochlore, kagome, and triangular lattices [17,18], but magnetic frustration also may emerge in the absence of geometrical frustration due solely to competing long-ranged exchange interactions. Experimental examples in tetragonal

systems have been identified recently in Ce-based metals with noncollinear magnetic structures, such as CeRhIn₅ and CeAgBi₂ [19,20]. A complete understanding of exchange-driven magnetic frustration in transition-metal-based systems without geometrical frustration is, however, still elusive and the question of whether there is a universal way of modeling it in itinerant systems remains unanswered. Magnetic frustration has been proposed to be an important ingredient to describe Fe-based materials [21] and, therefore, the “143” orthorhombic structure and its derivatives may be a good platform to address this question.

Chemical substitution studies together with the investigation of similar parent compounds often provide important insights on the nature of the magnetism in structurally related systems. Previous studies on Ca(Fe_{1-x}Co_x)₄As₃ ($0 \leq x \leq 0.32$) grown in Sn flux showed a slow suppression of the IC-SDW state with x , whereas the IC-C transition rapidly disappeared for $x > 0.1$ [22]. Single crystals with $x > 0.32$ could not be synthesized, which was suggested to be caused by the solubility limit for the 143 structure. We note, however, that the presence of a stable binary compound such as CoSn₂ could be detrimental to the formation of the Co 143 analog, and other fluxes may solve this issue.

Here, we report the synthesis of CaCo₅As₃ using indium flux. CaCo₅As₃ shares the same orthorhombic structure of CaFe₄As₃ but has an additional transition-metal site filling the “holes” between Ca atoms. This Co-based compound orders below $T_M = 16$ K in a magnetic state that cannot be ascribed to a simple magnetic structure. CaCo₅As₃ is a good metal at low temperatures and applied pressures to 2.5 GPa suppress T_N at a rate of only -0.008 K/GPa. Electron-electron correlations are modest, as evidenced by a Sommerfeld coefficient (γ) of 70 mJ/mol_{f.u.} K². First-principles calculations show a complex three-dimensional band structure in which the magnitude of the magnetic moments depends on the local environment at each Co site. Our results support a scenario in which frustration, driven by competing exchange interactions, play a key role.

Single-crystalline samples of CaCo₅As₃ were grown by the In-flux technique. The mixture of elements was placed in an alumina crucible and sealed in a quartz tube under vacuum. The sealed tube was heated to 1000°C for 12 h and then cooled to 400°C at 6°C/h. The flux was then removed by centrifugation. The crystallographic structure was verified by single-crystal diffraction at room temperature. In addition, several samples were characterized by elemental analysis using a commercial energy dispersive spectroscopy (EDS) microprobe.

A Quantum Design superconducting quantum interference device and small-mass calorimeter that employs a quasi-adiabatic thermal relaxation technique were used to measure magnetic and specific heat properties of the crystals. The electrical resistivity was obtained using a low-frequency ac resistance bridge and a four-contact configuration. Needlelike crystals were mounted in a hybrid piston-cylinder pressure cell with Daphne oil 7373 as the pressure medium. The change in T_c of a piece of Pb served as a manometer. The electronic structure was calculated using density functional theory with an all electron full potential linearized augmented plane wave method with local orbitals. Calculations were implemented in the code WIEN2K using a generalized gradient approximation

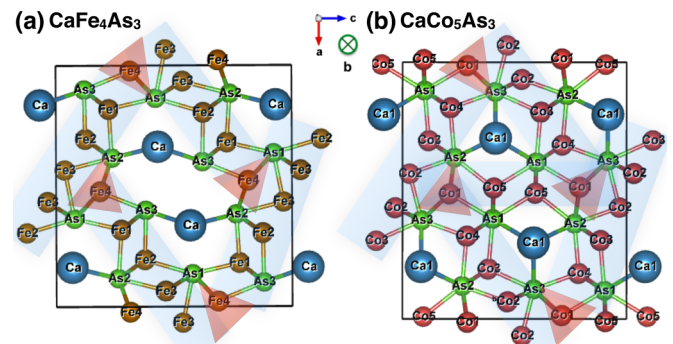


FIG. 1. Crystal structures of (a) CaFe₄As₃ [6] and (b) CaCo₅As₃ (this work). The elements Ca, Co, Fe, and As are represented by blue, red, gold, and green spheres.

[23,24]. Spin-orbit coupling was included for computing the density of states.

II. RESULTS

Figure 1 shows the orthorhombic crystal structure shared by CaFe₄As₃ [6] and CaCo₅As₃ (this work). In CaFe₄As₃, FeAs₄ tetrahedra form infinitely long segments along the b direction. In the ac plane, FeAs₄ tetrahedra strips containing structurally inequivalent Fe²⁺ ions [Fe(1), Fe(2), and Fe(3) sites in the blue region] are connected by fivefold Fe⁺¹ ions [Fe(4) site] to form a rectangular network that encloses two Ca atoms. Although the same crystal structure is realized in CaCo₅As₃, the “hole” between Ca atoms is filled by CoAs₄ tetrahedra at the Co(5) site, resulting in a more three-dimensional network with five inequivalent Co sites. We note that CaFe₅As₃ can be obtained via high-pressure synthesis and crystallizes in a monoclinic ($P2_1/m$) structure [25]. The physical properties of CaFe₅As₃ are unknown, but it is noteworthy that the Fe- and Co-“153” compounds form in different structure types, whereas the Fe-143 and Co-153 materials crystallize in the same space group.

Table I summarizes the structural parameters of CaCo₅As₃ determined by single-crystal x-ray diffraction. The lattice parameters are close to those of CaFe₄As₃ [$a = 11.852(3)$ Å, $b = 3.7352(6)$ Å, $c = 11.5490(18)$ Å] and the volume of the unit cell increases by 0.5%, likely due to the additional transition-metal site.

Table II displays the atomic coordinates and equivalent displacement parameters for CaCo₅As₃. The site symmetries are identical to those found in CaFe₄As₃ and the atomic coordinates are also very similar. The refined occupancy of CaCo₅As₃ is 100% for all sites, in agreement with the microprobe result CaCo_{4.9(1)}As_{3.1(1)}.

Figure 2(a) shows the temperature-dependent magnetic response $M(T)/H$ to a field of 1 kOe applied parallel to the a axis (dark blue squares), b axis (red circles), and c axis (light blue triangles). These results are from zero-field-cooled samples. A clear peak at 16 K for $H \parallel b$ is characteristic of the onset of antiferromagnetic order. For $H \parallel a$ and $H \parallel c$, however, $M(T)/H$ is typical of ferromagnets at the same transition temperature. This clear difference suggests the presence of anisotropic magnetic interactions between Co spins with ferromagnetic and antiferromagnetic components.

TABLE I. Crystallographic data of CaCo_5As_3 determined by single-crystal x-ray diffraction.

Crystal system	Orthorhombic
Space group	$Pnma$ (62)
Temperature	296(2) K
Wavelength	0.71073 Å
$2\theta_{\min}$	2.49°
$2\theta_{\max}$	28.43°
Index ranges	$-16 \leq h \leq 16, -4 \leq k \leq 5, -14 \leq l \leq 14$
Formula weight	559.51
a (Å)	12.425(2)
b (Å)	3.8101(6)
c (Å)	10.8513(17)
Volume (Å ³)	513.71(14)
μ (Mo $K\alpha$) (cm ⁻¹)	16.348
Goodness of fit on F^2	1.019
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0222
$R_w(F_o^2)^b$	0.0495

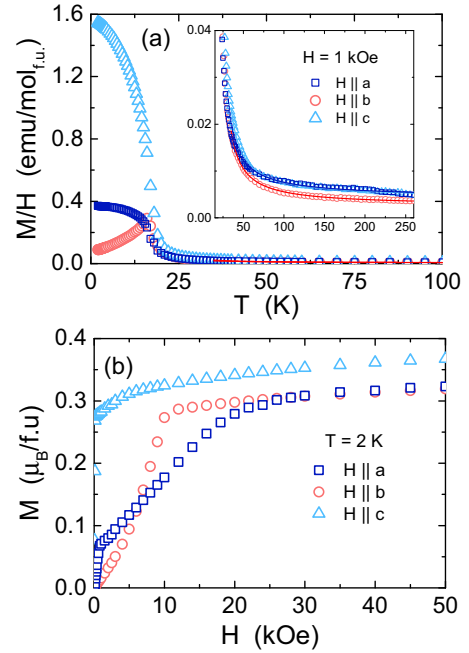
$$^a R(F) = \frac{\sum \|F_o\| - |F_c|}{\sum |F_o|}$$

$$^b R_w(F_o^2) = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w F_o^4} \right]^{1/2}$$

Above the ordering temperature where M is linear in H , $M/H \equiv \chi$, the uniform susceptibility. For all directions, $\chi(T)$ can be fit to a Curie-Weiss (CW) law plus a T -independent Pauli term, i.e., $\chi(T) = \chi_0 + C/(T - \theta)$, in the range from 35 to 350 K. The extracted values of χ_0 are 0.004(2) emu/mol_{f.u.} and 0.00257(3) emu/mol_{f.u.} for $H \parallel a, c$ and $H \parallel b$, respectively. The effective moment from these fits also is weakly anisotropic, 1.48(3) μ_B /f.u. ($H \parallel a, c$) and 1.38(1) μ_B /f.u. ($H \parallel b$), both of which are smaller than the theoretical value expected for Co^{2+} (3.87 μ_B using $J = S$). Naively, the effective moment per Co would be 0.26 μ_B (from one-fifth of a polycrystalline average of μ_{eff}) but, as we will come to later, the local environment and the hybridization between Co and As atoms are different for each Co site. From the CW fits, the Curie-Weiss temperatures are $\theta = 18(4)$ and 20(2) K for $H \parallel a, c$ and $H \parallel b$, respectively. These temperatures are identical within experimental error, positive, which is characteristic of dominant ferromagnetic interactions, and

TABLE II. Atomic coordinates and equivalent displacement parameters (Å²) for CaCo_5As_3 determined by single-crystal x-ray diffraction at room temperature. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	Wyck.	Occ.	x	y	z	U_{eq}
As(1)	4c	1	0.11107	0.25000	0.09824	0.005
As(2)	4c	1	0.12911	0.25000	0.73262	0.005
As(3)	4c	1	0.38532	0.25000	0.91474	0.005
Co(1)	4c	1	0.01244	0.25000	0.29001	0.008
Co(2)	4c	1	0.06633	0.25000	0.53238	0.005
Co(3)	4c	1	0.30513	0.25000	0.11698	0.005
Co(4)	4c	1	0.32191	0.25000	0.71380	0.005
Co(5)	4c	1	0.00960	0.25000	0.90666	0.006
Ca(1)	4c	1	0.29548	0.25000	0.41600	0.006

FIG. 2. (a) Temperature dependence of the magnetic response, $M(T)/H$, of CaCo_5As_3 in a field of 1 kOe applied along the a , b , and c axes. The inset shows the fits of the high-temperature data to a modified Curie-Weiss law. (b) Anisotropic field dependence of the magnetization at 2 K.

close in value to T_N , typically an indication of little, if any, frustration.

From these parameters that describe the uniform susceptibility, it would be reasonable to expect that CaCo_5As_3 could be a simple (Stoner-like) ferromagnet. As evidenced from the sharp peak in $\chi(T)$ for $H \parallel b$, this simple expectation obviously is incorrect, and the magnetic structure below 16 K must be more complex. A nontrivial magnetic structure is further reflected in the magnetization as a function of magnetic field, shown in Fig. 2(b). For $H \parallel a$, the magnetization initially increases quickly, as expected for a soft ferromagnetic, but instead of continuing smoothly to saturation, there is a clear anomaly in $M_a(H)$ at ~ 0.8 kOe, pointing to a change in magnetic structure. At higher fields, $M_a(H)$ smoothly approaches a regime in which it has a small but finite slope $dM/dH = 0.0053$ emu/mol_{f.u.} that is about 1.5 times larger than χ_0 for this orientation. We note that $M_c(H)$ has a similar high-field finite slope. When $H \parallel b$, $M_b(H)$ increases monotonically at low fields and crosses M_a . At 10 kOe, there is a kink in $M_b(H)$, possibly indicating a change in magnetic structure above which dM/dH approaches a constant value of 0.0063 emu/mol_{f.u.} that is about 2.5 times larger than χ_0 . These values of dM/dH above 35 kOe suggest either that the conduction band density of states at the Fermi energy (N_{E_F}) has been Zeeman split (by about 0.2 meV) to give a N_{E_F} that is 1.5–2.5 times larger than at low fields or that there may be one or more additional changes in magnetic structure at fields above 50 kOe. From magnetization and susceptibility measurements, the most likely scenario is that CaCo_5As_3 adopts a nontrivial ferrimagnetic order in zero applied field and that its structure is susceptible to field-induced changes.

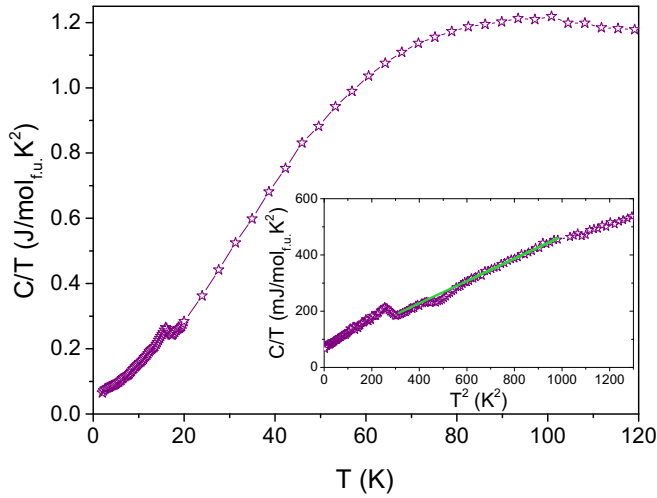


FIG. 3. Specific heat data as a function of temperature. The inset shows a linear fit (solid line) in a C/T vs T^2 plot.

We will return to this possibility, but clearly, high-field measurements as well as microscopic measurements (e.g., neutron diffraction and nuclear magnetic resonance) would be valuable to solve the magnetic structure of CaCo_5As_3 .

Specific heat data of CaCo_5As_3 also display a transition at 16 K (Fig. 3). Above the transition, a fit of the data to $C/T = \gamma + \beta T^2$ yields an electronic coefficient of $\gamma = 70 \text{ mJ/mol}_{\text{f.u.}} \text{K}^2$ (inset of Fig. 3). This value of γ should be taken with caution because of the rather small window (15 K) over which the fit was made. Nevertheless, the same fit below T_N also yields $\gamma = 70 \text{ mJ/mol}_{\text{f.u.}} \text{K}^2$, in surprising agreement with the high- T value. From these fits above and below T_N , entropy obviously is not conserved, suggesting that there may be another phase transition below the lowest temperature (2 K) of these measurements. Within the free-electron model, the Pauli susceptibility is defined as $\chi_p = \mu_B^2 N(E_F)$, where $N(E_F)$ can be obtained via $\gamma = (1/3)\pi^2 k_B^2 N(E_F)$. Here, μ_B is the Bohr magneton constant and k_B is the Boltzmann constant. Using the high- T experimental value of γ , the calculated Pauli susceptibility is $\chi_p = 1.3 \times 10^{-3} \text{ emu/f.u.}$, which is smaller than the values of χ_0 obtained from the magnetic susceptibility (2.6×10^{-3} and $3.7 \times 10^{-3} \text{ emu/f.u.}$ for $H \parallel b$ and $H \perp b$, respectively). This simple comparison between χ_p and χ_0 implies that $\chi_0/\gamma > 1$ and suggests that the conduction electrons have ferromagnetic (FM) correlations above T_N .

As shown in Fig. 4(a), the temperature dependence of the electrical resistivity, $\rho(T)$, of CaCo_5As_3 along the b axis displays metallic behavior and a curvature that is likely due to scattering of conduction electrons by phonons and s - d interband scattering. The low- T data display a clear kink at T_N , followed by a decrease due to the decrease in spin disorder scattering. The resistance ratio $\rho_{300 \text{ K}}/\rho_{2 \text{ K}} \sim 25$ is five times larger than that in the Fe-143 counterpart and indicates good crystallinity.

As in CaFe_4As_3 [7], there is a Fermi-liquid regime below 15 K where $\rho(T) = \rho_0 + AT^2$ yields a straight line in a ρ vs T^2 plot [bottom inset of Fig. 4(a)]. The extracted values are $\rho_0 = 4.9 \mu\Omega \text{ cm}$ and $A = 0.021 \mu\Omega \text{ cm K}^{-2}$. The corresponding Kadowaki-Woods (KW) ratio is $A/\gamma^2 = 9a_0$,

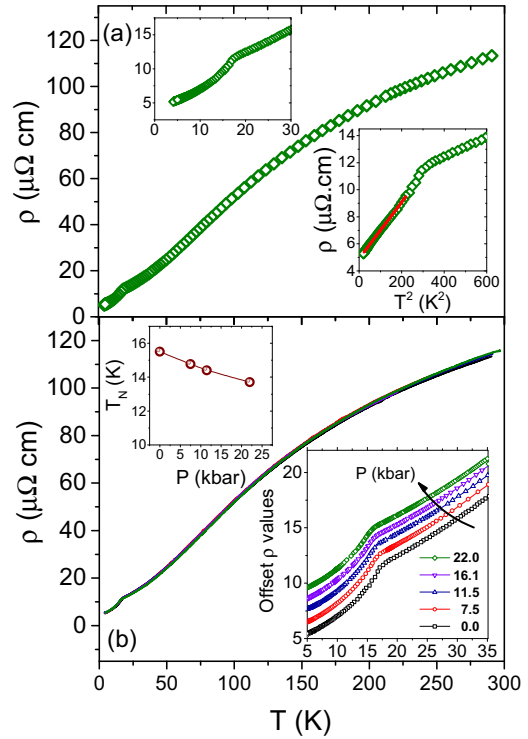


FIG. 4. (a) Electrical resistivity along the b axis, $\rho_b(T)$, of CaCo_5As_3 as a function of temperature. The insets plot the low-temperature resistivity vs T and T^2 . (b) Pressure dependence of $\rho_b(T)$. The left inset shows the pressure dependence of T_M . The right inset shows the low- T data for various pressures.

where $a_0 = 10^{-5} \Omega \text{ cm mol}_{\text{Co}}^2 \text{K}^2 \text{J}^{-2}$ is a universal value observed in strongly correlated materials. This ratio (A/γ^2) is about six times smaller than that for CaFe_4As_3 , and, not surprisingly, χ_0 is about four times and γ about 1.4 times smaller in CaCo_5As_3 compared to CaFe_4As_3 [7]. Together, these suggest that electronic correlations are present but not as strong in CaCo_5As_3 as they are in isostructural CaFe_4As_3 .

To investigate whether the magnetic order of CaCo_5As_3 can be suppressed to zero temperature, we measured its electrical resistivity as a function of applied pressure. Figure 4(b) shows that the overall temperature dependence of $\rho_b(T)$ does not change significantly with applied pressure. A closer look at the low-temperature region, however, shows that the magnetic transition temperature decreases smoothly as a function of pressure [bottom inset of Fig. 4(b)]. The rate of suppression is rather low ($\sim -0.008 \text{ K/GPa}$) and higher pressures are necessary to fully suppress the magnetic order.

Electronic structure calculations lend additional support to conclusions drawn from experiments and highlight differences between CaCo_5As_3 and CaFe_4As_3 . Figure 5 displays the density of states of CaCo_5As_3 as a function of energy, for which there is a finite density of states at the Fermi level contributed by all five of the Co ions. The associated band dispersion, plotted in Fig. 6(b), is notably three dimensional, and, in particular, planarlike sheets parallel to the b axis present in CaFe_4As_3 are absent in our material. From the solely itinerant electron calculations that ignore Coulomb interactions, the calculated $N(E_F) = 14 \text{ states/(f.u. eV)}$ is only about 45% of

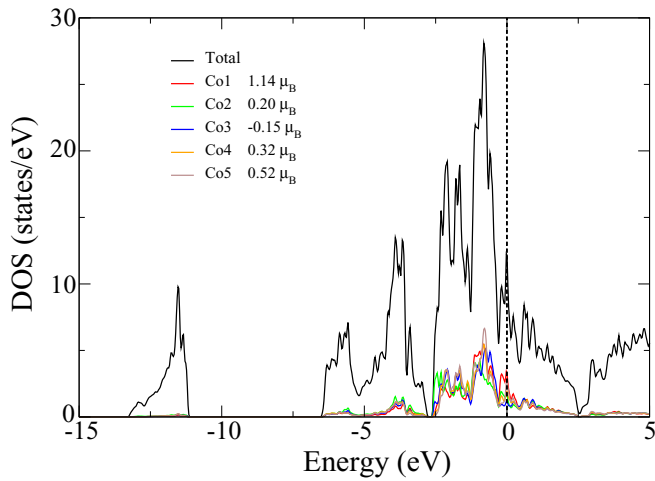


FIG. 5. Total density of states (DOS) as a function of energy as well as the partial contribution from each Co site for a nonmagnetically constrained calculation. The legend provides the moment on each Co site in a spin-polarized calculation.

the density of states obtained from heat capacity [$N(E_F) = 30$ states/(f.u. eV)], and is consistent with a nontrivial role of electronic correlations in CaCo_5As_3 .

As experimentally measured, the enhanced density of states also suggests a potentially magnetic state. Indeed, spin-polarized calculations find a magnetic ground state. The polarized band-structure calculations give distinct magnetic moments for each Co site [$1.14\mu_B$ on Co(1), $0.20\mu_B$ on Co(2), $-0.15\mu_B$ on Co(3), $0.32\mu_B$ on Co(4), and $0.52\mu_B$ on Co(5)], showing clearly that the moment depends on the local environment of each Co site. Further, these calculations anticipate ferrimagnetic order, as argued from magnetic susceptibility and magnetization measurements to be the likely ordered structure.

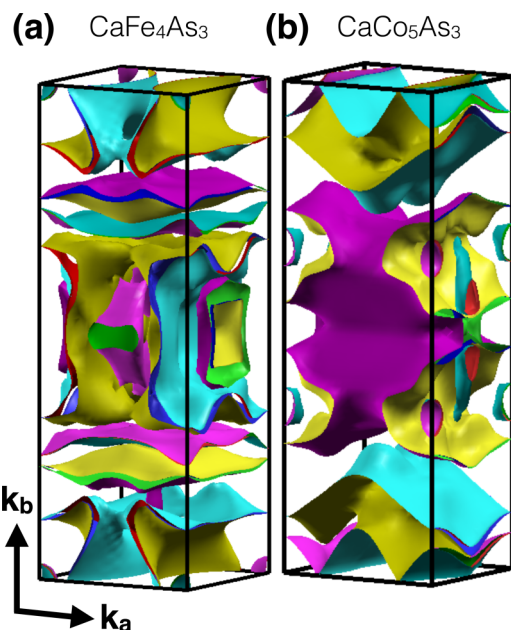


FIG. 6. Fermi surface of (a) CaFe_4As_3 and (b) CaCo_5As_3 .

As mentioned in the Introduction, the Fe moment in the Fe-based superconductors is sensitive to the Fe-As hybridization and tends to increase with increasing Fe-As distance. This tendency is recreated in CaCo_5As_3 , as the largest magnetic moment is observed at the site with the largest Co-As distance (Co1). The Co-As distances vary from $2.37(6)$ Å for Co2-5 up to 2.66 Å for Co1. Further, the bond angles Co-As-Co are closer to 90° for nearest neighbors than for next-nearest neighbors, indicating that nearest neighbors have parallel spins and next-nearest neighbors have antiparallel spins. This effect is in agreement with the observed ferromagnetic component and, as in FeAs, is consistent with the Goodenough-Kanamari rules that arise when local-moment physics is present. Thus, our results point to a scenario in which competing exchange interactions in a FM background drive magnetic frustration. This scenario explains the smooth pressure-dependent decrease of T_N because applied pressure is known to increase the hybridization by decreasing the lattice parameters. It will be interesting to investigate whether higher pressures will continuously drive the system to a quantum critical point giving rise to a quantum spin-liquid state. Another possible scenario is that pressure will relieve frustration, resulting in an increase of T_N or a change in the magnetic ground state.

The intricate structure of CaCo_5As_3 is further reflected in its Fermi surface, shown in Fig. 6(b). For comparison, we also computed the Fermi surface (FS) of CaFe_4As_3 using the structure determined by Ref. [8]. The FS of CaFe_4As_3 shown in Fig. 6(a) is in good agreement with that from Ref. [8]. The main difference between the Fermi surfaces of CaFe_4As_3 and CaCo_5As_3 is the absence of sheets parallel to the b axis in the Co counterpart. Because CaCo_5As_3 has one additional Co atom filling the “hole” in the crystal structure, the striplike structure previously seen in CaFe_4As_3 is now missing and, as a consequence, no clear sign of “visual” nesting is observed in CaCo_5As_3 . We speculate that the three dimensionality observed in CaFe_4As_3 and CaCo_5As_3 is likely responsible for the absence of superconductivity in these materials.

III. CONCLUSIONS

In summary, we have synthesized single crystals of CaCo_5As_3 , a transition-metal pnictide compound. CaCo_5As_3 is a metallic magnet ($T_M = 16$ K) with a moderate enhancement in electronic correlations. Its complex magnetic response indicates competing exchange interactions and magnetic frustration. Electrical resistivity measurements under pressure to 25 kbar show a smooth decrease in T_M to 14 K. Experiments at higher pressures and neutron diffraction measurements will be valuable to fully suppress the magnetic order and to solve the magnetic structure of CaCo_5As_3 , respectively.

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- [1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).
- [2] M. Rotter, M. Tegel, and D. Johrendt, *Phys. Rev. Lett.* **101**, 107006 (2008).
- [3] S.-Y. Xu *et al.*, *Science* **349**, 613 (2015).
- [4] L. X. Yang *et al.*, *Nat. Phys.* **11**, 728 (2015).
- [5] B. Q. Lv *et al.*, *Nat. Phys.* **11**, 724 (2015).
- [6] I. Todorov *et al.*, *J. Am. Chem. Soc.* **131**, 5405 (2009).
- [7] L. L. Zhao, T. Yi, J. C. Fettinger, S. M. Kauzlarich, and E. Morosan, *Phys. Rev. B* **80**, 020404(R) (2009).
- [8] Y. Nambu, L. L. Zhao, E. Morosan, K. Kim, G. Kotliar, P. Zajdel, M. A. Green, W. Ratcliff, J. A. Rodriguez-Rivera, and C. Broholm, *Phys. Rev. Lett.* **106**, 037201 (2011).
- [9] Z. P. Yin, K. Haule, and G. Kotliar, *Nat. Mater.* **10**, 932 (2011).
- [10] W. Bao, Y. Qiu, Q. Huang, M. A. Green, P. Zajdel, M. R. Fitzsimmons, M. Zhernenkov, S. Chang, M. Fang, B. Qian, E. K. Vehstedt, J. Yang, H. M. Pham, L. Spinu, and Z. Q. Mao, *Phys. Rev. Lett.* **102**, 247001 (2009).
- [11] S. A. J. Kimber *et al.*, *Nat. Mater.* **8**, 471 (2009).
- [12] E. Granado, L. Mendonca-Ferreira, F. Garcia, G. de M. Azevedo, G. Fabbris, E. M. Bittar, C. Adriano, T. M. Garitezi, P. F. S. Rosa, L. F. Bufaical, M. A. Avila, H. Terashita, and P. G. Pagliuso, *Phys. Rev. B* **83**, 184508 (2011).
- [13] C. Y. Moon and H. J. Choi, *Phys. Rev. Lett.* **104**, 057003 (2010).
- [14] M. Kenzelmann, A. B. Harris, S. Jonas, C. Broholm, J. Schefer, S. B. Kim, C. L. Zhang, S. W. Cheong, O. P. Vajk, and J. W. Lynn, *Phys. Rev. Lett.* **95**, 087206 (2005).
- [15] M. Kenzelmann, A. B. Harris, A. Aharony, O. Entin-Wohlman, T. Yildirim, Q. Huang, S. Park, G. Lawes, C. Broholm, N. Rogado, R. J. Cava, K. H. Kim, G. Jorge, and A. P. Ramirez, *Phys. Rev. B* **74**, 014429 (2006).
- [16] S. Zhao, J. M. Mackie, D. E. MacLaughlin, O. O. Bernal, J. J. Ishikawa, Y. Ohta, and S. Nakatsuji, *Phys. Rev. B* **83**, 180402(R) (2011).
- [17] J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, *Rev. Mod. Phys.* **82**, 53 (2010).
- [18] S. Nakatsuji, Y. Nambu, H. Tonomura, O. Sakai, S. Jonas, C. Broholm, H. Tsunetsugu, Y. Qiu, and Y. Maeno, *Science* **309**, 1697 (2005).
- [19] D. Fobes *et al.* (unpublished).
- [20] S. M. Thomas, P. F. S. Rosa, S. B. Lee, S. A. Parameswaran, Z. Fisk, and J. Xia, *Phys. Rev. B* **93**, 075149 (2016).
- [21] Q. Si and E. Abrahams, *Phys. Rev. Lett.* **101**, 076401 (2008).
- [22] L. L. Zhao, S. K. Kim, G. T. McCandless, M. S. Torikachvili, P. C. Canfield, J. Y. Chan, and E. Morosan, *Phys. Rev. B* **84**, 104444 (2011).
- [23] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Technische Universität Wien, Austria, 2001).
- [24] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [25] T. Stürzer, C. Hieke, C. Löhnert, F. Nitsche, J. Stahl, C. Maak, R. Pobel, and D. Johrendt, *Inorg. Chem.* **53**, 6235 (2014).