

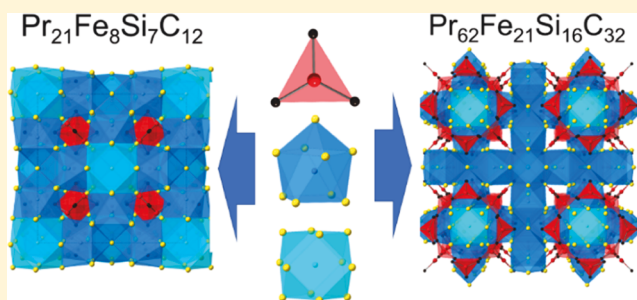
Pr₆₂Fe₂₁M₁₆C₃₂ Versus Pr₂₁Fe₈M₇C₁₂ (M = Si, P; M' = Si, Ge, Sn): Competing Intermetallic Carbides Grown from a Pr/Ni Flux

Tate O. Engstrand and Susan E. Latturer*

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306, United States

Supporting Information

ABSTRACT: Reactions of silicon, carbon, and iron in a low-melting flux mixture of praseodymium and nickel produced two competing intermetallic compounds. Pr₆₂Fe₂₁Si₁₆C₃₂ has a new structure type in tetragonal space group *P4/mmm* (*a* = 15.584(2) Å, *c* = 11.330(1) Å, *Z* = 1) that features trigonal planar FeC₃ units that share corners to form a framework of cylindrical channels encompassing a network of silicon-centered praseodymium clusters. Slight variation of reactant ratio and heating profile produced Pr₂₁Fe₈Si₇C₁₂ instead; this compound has the previously reported cubic La₂₁Fe₈Sn₇C₁₂ structure type. Identical Pr/Si clusters and FeC₃ subunit motifs are found in both structure types. In addition to reactant ratio and heating profile, size effects play a role in determining which structure forms. Replacing silicon with smaller phosphorus atoms produces only the tetragonal structure; replacement with larger elements (*M* = Ge, Sn) yields only cubic Pr₂₁Fe₈M₇C₁₂. Magnetic susceptibility measurements on single crystals of Pr₆₂Fe₂₁Si₁₆C₃₂ indicate antiferromagnetic ordering of the Pr moments below 17 K and no magnetic moment on iron atoms. The behavior of Pr₂₁Fe₈Si₇C₁₂ is more complex, revealing magnetic contributions from both Pr and Fe atoms and possible spin frustration.



■ INTRODUCTION

Intermetallic carbides are known for their tensile strength, exemplified in tungsten carbide and in the many varieties of steel, and their magnetic properties, as seen with the R₂T₁₄C (*R* = rare earth; *T* = Fe, Co, Ni) family of compounds.¹ However, the development of the field of intermetallic carbides has been slow relative to that of ternary intermetallics containing other main group elements.² Of the ~60 R_xT_yC_z structures known by 2006, most contain C₂ or C₃ linear chains.³ The remaining compounds, containing monoatomic C^{4−} species, have been classified by the Jeitschko group into two main categories based on their stoichiometric metal-to-carbon ratios.³ Those with low ratios (≤2) are termed carbometalates; those with high ratios (≥4) are metal-rich carbides. The latter may be thought of as interstitial compounds, with carbons often only partially occupying their positions. As compositions such as R₂Fe₁₄C (*R* = Pr, Sm, Gd–Tm, Lu)⁴ and ThFe₁₁C_{2–x} (1.5 ≤ *x* ≤ 2)⁵ suggest, the intermetallic character of these compounds dominates the physical properties, and the extensive transition-metal networks found in their structures often lead to interesting magnetic properties.

Carbometalates, on the other hand, feature little-to-no transition-metal bonding. Instead, transition-metal atoms are coordinated by carbon atoms. These TC_x units can be isolated from one another by surrounding rare earth atoms, as seen in La_{3.67}TC₆. They can also corner- or edge-share through bridging carbons to form polyanionic networks in 0–3

dimensions.⁶ Sc₃FeC₄ contains edge-sharing square planar [FeC₄]^{9−} clusters which propagate in one dimension parallel to the *b* axis. The ruthenium–carbon sublattice in GdRuC₂ forms two-dimensional layers separated by layers of Gd atoms, these layers stacking alternately in the *c* direction.⁷ Similar buckled sheets of Mo and C atoms are found in the material Pr₂Mo₂C₃, though carbons bridge the layers, making the Mo–C sublattice fully three-dimensional.³ T–C covalent bonding and the lack of T–T bonding typically eliminates transition-metal magnetic moments in carbometalates; however, other interesting properties may be present, including semiconductivity in LaRhC₂ and CeRhC₂,⁸ soft ferromagnetism in Gd₂OsC₂ and Tb₂OsC₂,⁹ and superconductivity in Y₂FeC₄,¹⁰ La_{1–x}Th_xNiC₂,¹¹ and LaNi₂B₂C.¹²

Expansion of research into quaternary phases (R_xT_yM_uC_z, with *M* = main group elements) promises one route to the development of materials with 2 ≤ (*x* + *y*)/*z* ≤ 4, between the metal-to-carbon ratios of the carbometalate and metal-rich carbide classifications. In this work, metal flux reactions of Fe, C, and either Si or P in a Pr/Ni melt (75:25% molar ratio) yielded the intermetallic phases Pr₆₂Fe₂₁M₁₆C₃₂ (*M* = Si, P). These compounds have a novel tetragonal structure containing corner-sharing FeC₃ subunits. This forms a zeolite-like iron carbide framework filled with a cationic Pr/*M* network. Some of these structural building blocks are also seen in a competing

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Table 1. Crystallographic Data and Collection Parameters for $\text{Pr}_{62}\text{Fe}_{21}\text{M}_{16}\text{C}_{32}$ ($\text{M} = \text{Si}, \text{P}$) and $\text{Pr}_{21}\text{Fe}_8\text{M}'\text{C}_{12}$ ($\text{M}' = \text{Si}, \text{Ge}, \text{Sn}$)

formula	$\text{Pr}_{62}\text{Fe}_{20.72}\text{Si}_{16.28}\text{C}_{32}$	$\text{Pr}_{61.90}\text{Fe}_{20.68}\text{P}_{16.32}\text{C}_{32}$	$\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$	$\text{Pr}_{21}\text{Fe}_8\text{Ge}_7\text{C}_{12}$	$\text{Pr}_{21}\text{Fe}_8\text{Sn}_7\text{C}_{12}$
formula wt (g mol^{-1})	10734.95(5)	10766.89(4)	3746.54(2)	4058.36(6)	4380.92(5)
crystal system	tetragonal	tetragonal	cubic	cubic	cubic
space group	$P4/mmm$	$P4/mmm$	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$
a (Å)	15.584(2)	15.450(4)	15.839(2)	15.896(2)	16.2565(8)
c (Å)	11.330(1)	11.314(3)			
Z	1	1	4	4	4
volume (Å ³)	2751.5(7)	2701(2)	3973(1)	4017(2)	4296.2(6)
calc. density (g cm^{-3})	6.479(2)	6.620(4)	6.263(2)	6.711(3)	6.773(1)
index ranges	$-20 \leq h \leq 20$ $-20 \leq k \leq 20$ $-14 \leq l \leq 14$	$-20 \leq h \leq 19$ $-20 \leq k \leq 20$ $-15 \leq l \leq 15$	$-21 \leq h \leq 20$ $-21 \leq k \leq 20$ $-20 \leq l \leq 21$	$-21 \leq h \leq 20$ $-21 \leq k \leq 20$ $-20 \leq l \leq 21$	$-20 \leq h \leq 20$ $-19 \leq k \leq 20$ $-21 \leq l \leq 21$
theta range (deg)	1.307–28.509	1.318–28.612	2.227–28.490	2.219–28.378	2.170–28.452
reflections collected	32 217	31 760	10 639	11 385	10 453
unique data/parameters	2021/101	1996/113	301/23	301/15	326/18
μ (mm^{-1})	29.640	30.208	28.201	32.819	29.862
R_1/wR_2	0.0202/0.0398	0.0188/0.0346	0.0148/0.0374	0.0303/0.1562	0.0155/0.0327
R_1/wR_2 (all data)	0.0217/0.0442	0.0207/0.0379	0.0150/0.0374	0.0307/0.1564	0.0164/0.0331
residual peak/hole ($\text{e}^- \text{Å}^{-3}$)	2.930/−1.396	2.453/−1.701	1.590/−1.022	3.779/−5.455	2.367/−1.424

byproduct, $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$, a new analog of the previously reported cubic $\text{La}_{21}\text{Fe}_8\text{Sn}_7\text{C}_{12}$ structure.⁷ Magnetic susceptibility measurements and band structure calculations for $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ indicate that the iron atoms in the compound are not magnetic; the low temperature complex antiferromagnetic ordering is due to the Pr^{3+} ions. Conversely, both iron and praseodymium moments contribute to the magnetic behavior of $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$.

EXPERIMENTAL PROCEDURE

Synthesis. Praseodymium ingots, nickel slugs, and red phosphorus powder were obtained from Alfa Aesar (99.9% for all except P, at 99%); iron, silicon, germanium, and carbon powders were obtained from Strem Chemicals (99.9%); and tin powder was obtained from Cerac, Inc. (now Materion, 99.8%). Reagents were used as received, and were stored and handled under argon atmosphere. The Pr/Ni binary mixture used as the reaction flux was prepared by arc-melting a 75:25% mole ratio of Pr and Ni under argon on a water-cooled copper hearth, turning the ingot over several times and re-melting to ensure a homogeneous mixture of the metals. Inspection of the Pr/Ni phase diagram shows that this mole ratio forms the congruently melting compound Pr_3Ni (mp 525 °C) on cooling.¹³ The resulting brittle Pr/Ni ingot was crushed into pieces up to 1 mm diameter for use in subsequent reactions.

Reaction mixtures were prepared in alumina crucibles. For reactions involving Si, the Fe, Si, and C powders and crushed Pr/Ni mixture were weighed to obtain Pr/Ni/Fe/Si/C mmol ratios of 9.5:2.8:0.7:0.7:1.8; reactions involving phosphorus were performed with Pr/Ni/Fe/P/C mmol ratios of 9.4:2.9:0.7:0.8:1.2. Germanide reactions were performed with Pr/Ni/Fe/Ge/C mmol ratios of 9.4:3.0:3.2:0.9:1.7. For reactions with tin, mmol reagent ratios of 9.5:3.0:0.9:0.7:1.2 were used for elements Pr/Ni/Fe/Sn/C.

Powders of iron, carbon, and the main group element were sandwiched between two layers of flux mixture, approximately 0.8 g (top layer) and 0.7 g (bottom layer). The loaded crucible was placed on top of a tuft of quartz wool resting at the bottom of a quartz sleeve. An iron mesh frit was placed on top of the crucible, and another tuft of quartz wool placed on top of the frit, the frit and wool making it possible to separate the molten flux from the reaction products during centrifugation. The reaction vessel was removed from the argon atmosphere and placed on a vacuum line under 60 mTorr and flame-sealed. The sealed ampoule was placed in a furnace and heated to 950 °C for 4 h, soaked at 950 °C for 20 h, then cooled to 625 °C over the next 72 h. At the end of the heating profile, the ampoule was removed

from the oven, inverted, and centrifuged for 2 min to decant the molten flux.

Elemental Analysis. Elemental analysis was performed using an FEI Nova 400 scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS) capability. Single crystals of products were mounted on carbon tape affixed to an aluminum puck with flat surfaces oriented normal to the electron beam. The accelerating voltage was set to 30 kV with an accumulation time of 30 s. Data collected on the surface and interior of cleaved crystals of the tetragonal $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ compound gave average molar ratios for Pr/Fe/Si of 64(1):22(1):14(1)%. A similar analysis of cubic $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ crystals indicated Pr/Fe/Si molar ratios of 59(4):22(1):19(5)%. Nickel and aluminum were found to be present in trace amounts (<2.0%). The Ni is likely present as flux residue on the crystal surface, though it may also substitute on Fe sites in small amounts. Aluminum was likewise regarded as a possible minor contaminant on Si sites. Carbon content cannot be determined by EDS analysis. The presence of this element is implied because of its use as a reactant, the observation of electron density peaks in the single-crystal X-ray data refinement, and the presence of characteristic iron–carbon bond lengths observed in the structure. Measurements of cubic crystals from the Ge-including reactions gave Pr/Fe/Ge at. % ratios of 58.2(7):21.5(8):20.3(7); and tetragonal products from P-including reactions measured 62(1):24.9(8):13.4(4)% in Pr, Fe, and P. Elemental compositions are consistent with the cubic and tetragonal phase stoichiometries determined by crystallographic studies.

Crystallographic Studies. Single crystals of the Pr/Fe/M/C products were mounted on glass fibers using epoxy. Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX2 CCD diffractometer at room temperature, using a Mo-target X-ray tube ($\lambda = 0.71073$ Å). Data were collected as ω scans with 0.5° step width and integrated with the Bruker SAINT software. The $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ structure was refined in the space group $P4/mmm$ (no. 123) and the $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ structure in space group $Fm\bar{3}m$ (no. 225). Least-squares refinement was performed on $|F^2|$ using the SHELX software package, version 2014/3.¹⁴ Praseodymium and iron atoms were located via direct methods, and the silicon and carbon peaks were determined from residual electron density peaks in difference Fourier maps. Light elements were further verified through analysis of interatomic bond lengths. Occupancies were assigned based on elemental analysis, bond lengths, and consideration of coordination environments (see discussion). Any remaining peaks in the electron density maps were located very close to heavy atoms and were deemed unlikely to correspond to actual atoms. Crystallographic data collection parameters for these compounds and their analogs are summarized

in Table 1. Further crystallographic data (atomic positions, site occupancy factors, and thermal parameters) are found in the Supporting Information (Tables S1 and S2).

Magnetic Susceptibility Measurements. Magnetic properties were investigated using a Quantum Design MPMS SQUID magnetometer. A single large crystal of $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ was sandwiched between two 4 cm pieces of Kapton tape and then placed inside a plastic sample holder for insertion into the magnetometer. Field-cooled (FC) and zero-field cooled (ZFC) measurements were collected along the a and c axes, at 500 G applied field strength over a temperature range of 1.8–300 K, and field-dependence data were collected from 0 to 70 000 G at both 5 and 50 K. To measure the $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ phase, seven single crystals were clustered together in random orientation on Kapton tape as before. FC and ZFC measurements were taken at 500 G over the temperature range 1.8–300 K. Field-dependence data were measured from 0 to 70 000 G at 2 K.

Electronic Structure Calculations. Density of states (DOS) calculations were performed using the tight-binding linear muffin tin orbitals-atomic sphere approximation^{15–17} implemented in the Stuttgart TB-LMTO-ASA software package (version 47.1b).¹⁸ The structural model was based on unit cell parameters and atomic coordinates experimentally determined by single crystal X-ray diffraction at 298 K for $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ and $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$. The TB-LMTO-ASA method is known to produce large charge oscillations in d and f orbitals in model systems with lanthanide and actinide atoms, leading to difficulty in convergence.¹⁹ Therefore, Pr atoms were modeled as La. In $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$, the partially occupied Pr(10) site was treated as fully occupied by La. There is also a mixed site Fe(4)/Si(5) which is ~33% occupied by Fe, ~66% by Si. Two test models were calculated, one treating this site as fully occupied by Fe and in the other fully occupied by Si. The overall stoichiometries of the model phases were therefore $\text{La}_{63}\text{Fe}_{22}\text{Si}_{15}\text{C}_{32}$ ("Fe-rich model") and $\text{La}_{63}\text{Fe}_{20}\text{Si}_{17}\text{C}_{32}$ ("Si-rich model"). Empty spheres were added to fill the interstitial spaces of the model unit cell. An improved tetrahedron method was used to integrate a $16 \times 16 \times 16$ k -space, giving 405 irreducible k points in the first Brillouin zone for each model of the tetragonal phase and 145 irreducible k points for the cubic phase. The basis sets for all calculations consisted of $6s/(6p)/5d/4f$ for La, $4s/4p/3d$ for Fe, $3s/3p/(3d)$ for Si, and $2s/2p/(3d)$ for C, with parenthetical orbitals downfolded.

RESULTS AND DISCUSSION

Synthesis. $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ was obtained from reactions of iron, silicon, and carbon in a Pr/Ni (75:25%) binary flux mixture. The reaction procedures reported here allow for growth of relatively large crystals in the form of silvery square plates (Figure 1a) of up to 1 mm in length with up to 0.5 mm thickness. In the SEM micrographs, droplets of flux residue can be seen on the surface of the crystals. This residue quickly oxidizes on exposure to air, with granules of green powder lifting from the surface of the crystals. The initial oxidation of surface flux residue is followed by a slow degradation of the bulk phase, which occurs over a period of months for larger crystals. The crystals are stable in water for short periods of time but begin to deteriorate when left in water for a day. Etchants (1 M HCl, HNO_3 , and NaOH) were tested for their ability to remove surface impurities, but these solutions attack the bulk crystals as quickly as the surface flux. To obtain clean crystals for subsequent measurements, crystals were allowed to sit in air for weeks to allow the surface flux to oxidize. These crystals were then placed in individual vials and agitated vigorously to remove as much oxidized flux as possible. Crystals were then washed with hexanes to remove the remaining particles.

Solid products were analyzed by powder X-ray diffraction, indicating the presence of the dominant components β -Pr,

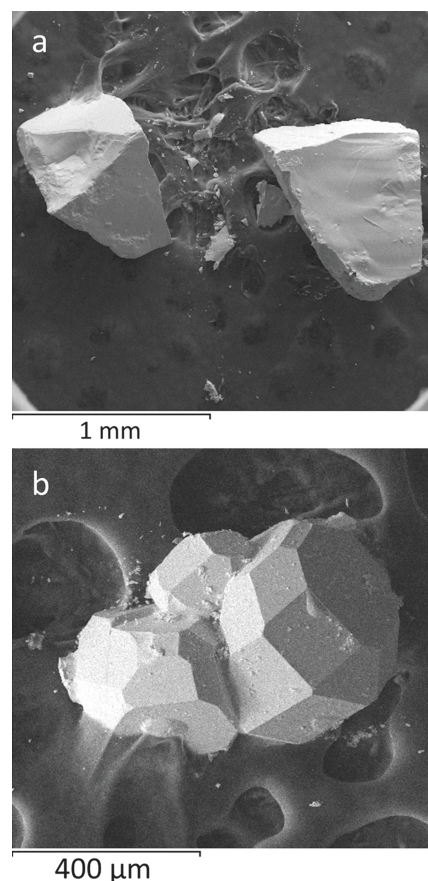


Figure 1. SEM images of flux-grown crystals of the (a) $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ and (b) $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ phases. Droplets of flux and flakes of minor byproducts can be seen on the surface of the germanide crystal.

$\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ and $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$. Minor byproducts seen in some reactions included $\text{Pr}_2\text{Fe}_{14}\text{C}$, Pr_5Si_3 , $\text{Pr}_6\text{Fe}_{13}\text{C}$, and $\text{Pr}_2\text{Fe}_{17}\text{C}$, with the latter observable as hexagonal rods in reactions using large amounts of Fe. The yield of the tetragonal phase $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ was optimized when reagent amounts of 12.5:4.1:0.8:0.8:1.8 mmol in Pr, Ni, Fe, Si, and C were heated to 950 °C for 3 h, held at this temperature for 12 h, then lowered over the course of 96 h to 700 °C, at which temperature the reactions were centrifuged. Figure 2 shows an X-ray powder pattern of solid products isolated from a flux reaction producing $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$. Analysis of the powder pattern indicates the presence of a large amount of β -Pr; at the

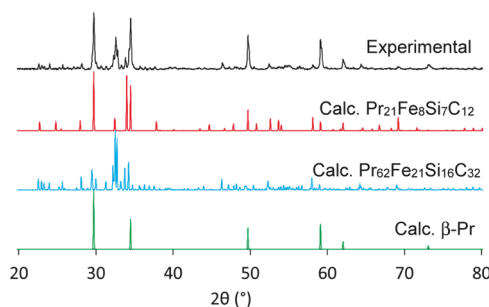


Figure 2. Experimental X-ray diffraction powder pattern for reaction targeting $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$. Calculated powder patterns for β -Pr and the title compounds are shown below the experimental powder pattern.

temperature of centrifugation it is highly viscous and solidifies before fully decanting, but it can be removed from products by allowing it to oxidize.

When the reaction was run with faster cool-down rates (-40 K/h), $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ was not observed. Reactions in which a dwell temperature was inserted at 850 °C between the maximum and decanting temperatures increased the cubic phase yield, as did increasing the relative amount of included silicon powder. The yield of $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ was maximized using 12.4:3.9:1.1:2.2:2.2 mmol amounts in Pr, Ni, Fe, Si, and C. Although the cubic phase was the predominant product, small amounts of $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$, and Pr_3Si_3 were also present, in addition to β -Pr. The increase in the cubic phase yield reflects its slightly higher silicon content relative to that of the tetragonal phase.

The cubic phase grows as well-faceted cuboids or truncated cubes, often with extensive agglomeration, though clustered crystals are easily separated with a razor blade (Figure 1b). Neither phase cleaves along lattice planes; breaks in the crystal resemble the fracturing of glassy materials. The cubic phase fractures easily, breaking to pieces with a touch of the edge of a razor blade. Breaking the tetragonal phase requires the application of greater force. Single-crystal cuboid specimens frequently grow to about 0.5 mm diameter.

$\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ and $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ have similar stoichiometries, with percent compositions in Pr/Fe/Si/C being 47.3:15.8:12.4:24.4% for the former structure and 43.8:16.7:14.6:25.0% for the latter. For the purposes of calculating the metal-to-carbon ratio, silicon is viewed as contributing to the metals. Whereas the silicon is likely anionic, they are separated by the rare earth cations from the T–C polyanionic network. With this consideration, both phases fall above the upper limit of the metal–carbon ratio for carbometalates ($x + y/z \geq 2$ for $\text{R}_x\text{T}_y\text{C}_z$) and below that for the metal-rich carbides ($x + y/z \geq 4$), with $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ and $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ metal–carbon ratios at 3.09 and 3.00, respectively. This correlates with the fact that their structures feature dimers and small clusters of transition metals, intermediate between the isolated transition metals in carbometalates and the networks in metal-rich carbides (vide infra).

Structure of $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$. Single crystal diffraction data sets for three separate crystals were used to confirm the structure of $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$. In each data set, three sites exhibited disorder: 2f ($0, 1/2, 0$), 2g ($0, 0, z$), and 1a ($0, 0, 0$). Each site is coordinated to surrounding Pr cations, with all three refinements suggesting 2f was either a partially occupied Pr site or a Pr/Si mixed site; the 1a site was either a partially occupied Pr or fully occupied Si site; and the 2g site a partially occupied Fe site or else a mixed Fe/Si site. These possible conditions were tested against each data set, until solutions were found that optimized the refinements. Eight symmetry equivalent Pr(1) atoms form a cube around the 2f position, at a distance of 3.46 Å. The 2f–Pr(1) distance is slightly shorter than bonds in Pr metal (3.65 Å)²⁰ but larger than the 3.23 Å Pr–Pr distances found in the Laves phase PrFe_2 .²¹ Pr–Fe bonds on the order of 3.3 Å have been measured in $\text{Pr}_2\text{Fe}_{17}$; the iron atom involved in this long bond is a corner-shared capping atom.²² The majority of Pr–Fe bonds in the $\text{Pr}_2\text{Fe}_{17}$ are closer to 3.1 Å, as is the 3.09 Å distance between Pr and Fe atoms in PrFe_2 .²¹ Pr–Si bonds range from the order of 3.0 Å in PrFeSi ²³ to about 3.2 Å in $Pnma$ PrSi .²⁴ The bond lengths

observed around position 2f suggest this site is occupied by Pr; the occupancy at this assignment was refined to 49.8%.

The 2g position is 2.46 Å from its symmetry equivalent, suggesting the placement of Fe or Si atoms. When assigned as an Fe atom, the position exhibits 67% occupancy and an unusually small thermal parameter ($1/2$ the size of the next smallest U_{eq} value). When the site is assigned as mixed Fe/Si atoms, the occupancy refines to 36% Fe, 64% Si with reasonable thermal parameters. The dimer of positions is surrounded by a pair of face-sharing square antiprisms defined by Pr atoms (see Figure 3c). The distance from 2g to surrounding Pr positions is 3.04 – 3.14 Å. These lengths agree with Pr–Fe and Pr–Si bond lengths in compounds such as PrFeSi_2 ²⁵ and PrFe_2Si_2 .²⁶

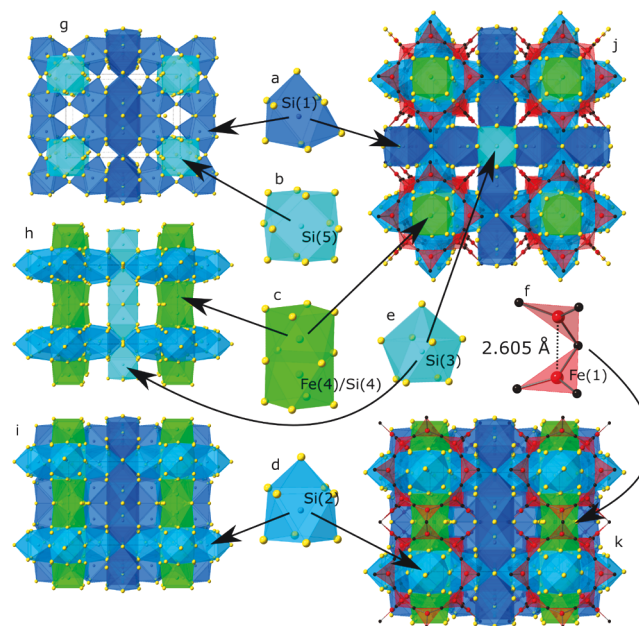


Figure 3. Overall structure, local environments, and cationic sublattices of $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$. Pr atoms are represented in yellow, Si in blue, Fe in red, and C in black. (a) $\text{Si}(1)@Pr_9$ tricapped trigonal prism. (b) $\text{Si}(5)@Pr_{12}$ cuboctahedron. (c) Face-sharing $X(4)@Pr_8$ square antiprisms ($X = \text{Fe}, \text{Si}$). (d) $\text{Si}(2)@Pr_9$ monocapped square antiprism. (e) $\text{Si}(3)@Pr_9$ monocapped square antiprism. (f) Dimer of corner-sharing FeC_3 clusters. (g) Sublattice formed from $\text{Si}(1)$ and $\text{Si}(5)$ and their surrounding Pr sites. (h) Sublattice formed from $\text{Si}(2)$, $\text{Si}(3)$, and $X(4)$ and surrounding Pr sites. (i) Combination of (g,h) taken together. (j) Overall structure, viewed along the c -axis. (k) Structure viewed along the a -axis.

Position 1a sits at the center of a slightly elongated cuboctahedron, with distances of 3.43 – 3.46 Å to the 12 surrounding Pr atoms. These distances suggest Pr–Pr contacts, but the peak intensity at this position is very low; a Pr would occupy only about $\sim 20\%$ of the position. The $\text{Ln}_{21}\text{Fe}_8\text{M}_7\text{C}_{12}$ structure features similar 12-coordinate cuboctahedral units, which in every case refine well with the main group element at the center.^{2,27,28} Given that the local coordinating environment is composed of a large number of electropositive rare earths, the atom at 1a is likely anionic. For these reasons, Si was assigned to position 1a; refinement indicated 88(4)% occupancy. The analogous P(4) position in the $\text{Pr}_{62}\text{Fe}_{21}\text{P}_{16}\text{C}_{32}$ analogue is 97(3)% occupied.

The structure of $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ is shown in Figure 3, with atom positions and thermal parameters given in Table S1. It

can be viewed as an anionic Fe–C framework interpenetrating with a cationic Pr–Si sublattice. The monomer of the Fe–C framework is the FeC_3 trigonal planar unit, which shares corners to form cylindrical channels centered on each unit cell edge. The Fe–C sublattice is bonded continuously in the c -axis direction; channels are also formed in the a and b directions along the unit cell edges. This is akin to the 3D networks formed from corner-sharing SiO_2 tetrahedra in zeolites. It is also similar to the 3D polyanionic network found in the carbometalate family LnRhC_2 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$), where distorted square planar RhC_4 monomers corner-share to form Ln-filled channels in each of the lattice directions,⁸ similar to the network of corner-sharing FeC_3 units seen in $\text{Gd}_{13}\text{Fe}_{10}\text{C}_{13}$.²⁹ Iron and carbon atoms in the $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ framework occupy four unique sites each, with Fe–C bond distances falling between the ranges of 1.830(6) and 1.94(1) Å. These distances straddle the Fe–C bond length observed in the carbometalates $\text{La}_{21}\text{Fe}_8\text{Sn}_7\text{C}_{12}$ (1.92 Å)² as well as cubic rare earth borocarbides $\text{Ce}_{33}\text{Fe}_{13.1}\text{Al}_{1.1}\text{B}_{24.8}\text{C}_{34}$ (1.917 Å) and $\text{Ce}_{33}\text{Fe}_{13}\text{B}_{18}\text{C}_{34}$ (1.947 Å)³⁰ and iron-aluminum carbon alloys such as Fe_3AlC (1.890 Å).³¹ The cylindrical channels about the c -axis are radially symmetric. The cross section of the channels along the a and b axes, however, are slightly elliptical, with the long axis of the ellipse parallel to the a -axis edges. Symmetry equivalent C(3) atoms all intersect at special positions on an ab mirror plane halfway between the c faces of the unit cell. Iron atoms in position Fe(1) are bridged by the C(3) atoms and are within a bonding distance of 2.605(2) Å to their symmetry equivalents (Figure 3f). This compares well with Fe–Fe bond lengths seen in $\text{La}_{21}\text{Fe}_8\text{Sn}_7\text{C}_{12}$ (2.55 Å), $\text{Y}_{15}\text{Fe}_8\text{C}_{25}$ (2.558–2.71 Å)³² and falls between those found in the metallic phases γ -Fe (2.425 Å) and ϵ - Fe_3C (2.754 Å),³³ suggesting the possibility of Fe(1)–Fe(1) magnetic coupling.

The $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ structure contains five unique silicon sites. The Si(1) and Si(2) sites at Wyckoff sites 8t and 4l, respectively, are both coordinated by nine Pr cations in tricapped trigonal prisms, with Pr–Si bond distances ranging from 3.039 to 3.499 Å for the former and 2.959–3.463 Å for the latter site. Centered on each unit cell vertex, four Si(2)@Pr₉ clusters corner-share to form fanlike structures parallel to the ab plane (see Figure 3h). The Pr atoms on the faces nearest the vertices form the 12-coordinate cuboctahedral cluster around the Si(5) position at the corners of the unit cell (Wyckoff site 1a, discussed above). The Si(3) site, Wyckoff position 2h, is coordinated by a monocapped square antiprism of nine surrounding Pr ions, with bond distances 3.134 and 3.229 Å to the Pr atom in the square antiprism and 3.524 Å to the capping praseodymium atom. A chain of these monocapped square antiprisms (Si(3)@Pr₉) runs through the center of the unit cell along the c -axis direction, alternately corner-sharing their capping atom and sharing the square faces opposite to the capping atom, as shown in Figure 3h.

The structure's mixed X(4) ($X = \text{Fe}, \text{Si}$) position—the 2g Wyckoff site—is 34(2)% occupied by iron. X-ray precession photos taken along the a and c axes of the crystal showed no evidence of supercell reflections; the mixed occupancy is therefore random. The X atom is coordinated to eight Pr atoms in a square antiprism geometry. Symmetry equivalents of site X(4) straddle the ab plane bisecting the c length of the unit cell, close enough to bring the occupants of the site within bonding distance (2.466(7) Å); this forms an overall X_2 @Pr₁₂ dimer of square antiprisms (Figure 3c) surrounding a dumbbell of X atoms. Given a statistical occupancy of the

site, about 46% of the X(4)–X(4) dimers in the extended structure are Si–Fe dimers, 41% Si–Si dimers, and 13% Fe–Fe dimers.

Structure of $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$. $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ is isostructural with previously reported $\text{RE}_{21}\text{T}_8\text{M}_7\text{C}_{12}$ ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}$; $\text{T} = \text{Mn}, \text{Fe}$; $\text{M} = \text{Si}, \text{Ge}, \text{Te}, \text{Sn}, \text{Pb}, \text{Bi}$) phases.^{2,27,28} The overall structure and important features are shown in Figure 4. The

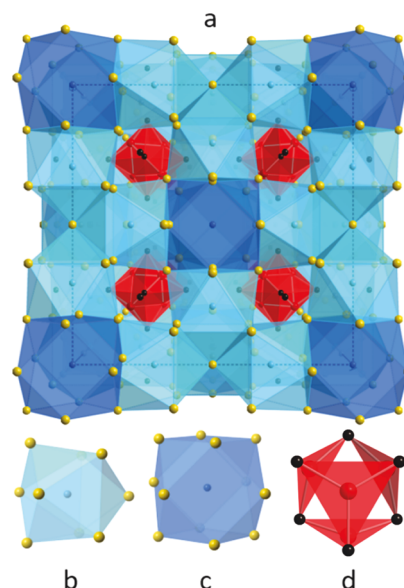


Figure 4. Structure and local environments for $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$. Yellow spheres represent Pr atoms, red spheres Fe, blue spheres Si, and black spheres C. (a) Unit cell viewed down the c -axis. (b) Tricapped trigonal prism Si(1)@Pr₉. (c) Si(2)@Pr₁₂ cuboctahedron. (d) Fe_4C_6 edge-capped tetrahedral cluster geometry.

cubic unit cell features eight tetrahedral iron clusters edge-capped by carbon atoms embedded in a Pr/Si framework. This Fe_4C_6 unit can also be described as four corner-sharing FeC_3 units (see Figure 4d). The Fe–Fe distances in the tetrahedron are 2.543(4) Å, a distance marginally longer than Fe–Fe interatomic distances found in elemental metal, (2.48–2.53 Å) and within the range of the Fe–Fe distances found in the tetragonal phase (2.47–2.60 Å). Edge-capping carbon atoms are 1.91(1) Å from each Fe, longer than the distances found in ϵ - Fe_3C (1.7–1.784 Å)³³ but shorter than found in the metal-rich carbide $\text{Pr}_2\text{Fe}_{14}\text{C}$ (2.033–2.098 Å).⁴ Likewise, the Fe–C distance in the cubic phase is between those found in the Fe–C sublattice of the tetragonal phase (1.834–1.94 Å). Each of the two crystallographically unique Si atoms are surrounded by Pr cations, suggesting the Si atoms are anionic. The Si(1) atom at the 24e Wyckoff position is coordinated by a monocapped square antiprism of nine Pr atoms (Figure 4b). The bond distances between Si(1) and the surrounding Pr atoms range from 3.151 to 3.257 Å. The Si(2) atom at the 4a Wyckoff position is found at the center of a cuboctahedron of 12 Pr atoms, with fairly long Si–Pr bonds of 3.593 Å (Figure 4c). These two silicon-centered clusters—Si(1)@Pr₉ and Si(2)@Pr₁₂—are directly comparable to those found in the tetragonal phase (Figure 3a,b) (Table 2).

Structural Comparison. Structural similarities between the two Pr/Fe/Si/C phases (corner-sharing FeC_3 units, Si@Pr₉ clusters, cuboctahedral Si@Pr₁₂ clusters), as well as their similar elemental ratios and occurrence as competing products, indicate possible interconversion between a kinetically

Table 2. Ranges of Interatomic Distances (Å) in Structures $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ and $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$

atom 1–atom 2	$\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$	$\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$
Pr–C	2.515(5)–2.686(1)	2.437(8)–2.708(6)
Pr–Fe	3.0982(6)–3.121(1)	2.921(1)–3.559(1)
Pr–Si	3.194(1)–3.311(3)	2.958(2)–3.463(4)
Pr–Pr	3.6116(7)–3.8682(5)	3.237(1)–4.0838(6)
Fe–C	1.896(6)	1.830(6)–1.94(1)
Fe–Fe	2.549(2)	2.466(7)–2.605(2)

stabilized phase (tetragonal $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$) and a more thermodynamically stable phase (cubic $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$). Attempts were made to carry out differential scanning calorimetry measurements on a scaled-down flux mixture (to observe crystallization events in situ); these were stymied by reaction with trace oxygen in the argon flow.

Another possible factor controlling structure formation is size effects. The cubic $\text{RE}_{21}\text{Fe}_8\text{M}_7\text{C}_{12}$ structures form in best yield with larger main group elements ($M = \text{Ge}, \text{Sn}$). Analogs of tetragonal phase $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ are only found with smaller M elements. Substituting P for Si in the Pr/Ni/Fe/M/C system yielded the compound $\text{Pr}_{61.90}\text{Fe}_{20.68}\text{P}_{16.32}\text{C}_{32}$ (see Table 1). Analogs were also found in preliminary explorations of the Ce/Fe/Al/C system ($a = 15.580(1)$ Å, $c = 11.3888(8)$ Å) and the Pr/Fe/S/C system ($a = 15.636(2)$ Å, $c = 11.378(1)$ Å).²⁸ The tetragonal structure has a higher ratio of small $M@R_9$ clusters to large $M@R_{12}$ clusters (14:1) compared to the cubic structure (6:1) and might be stabilized by smaller M elements. Flux growth of additional R/Fe/M/C systems are underway.

Magnetic Properties of $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ and $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$. Susceptibility measurements were performed on an oriented single crystal of $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ under an applied field of 500 G. Datasets were collected with the applied field along the a - and c -axes directions. The temperature dependence of the magnetic susceptibility (Figure 5a) shows paramagnetic behavior at high temperatures and a distinct cusp at 17 K for both orientations of the crystal, indicating a long-range antiferromagnetic ordering transition. Fitting the parameters of the Curie–Weiss law to the paramagnetic data for both orientations yields a magnetic moment per Pr^{3+} cation of $3.76 \mu_B$ (for $H_{//c}$ data) and $3.86 \mu_B$ (for $H_{\perp c}$ data). These values are only slightly larger than the expected moment for a free Pr^{3+} ion of $3.58 \mu_B$. If there is any contribution to the magnetic moment of this compound from the iron atoms, it is very small. This negligible magnetic contribution from iron is expected, given the hybridization with the surrounding carbon atoms and resulting highly delocalized nature of the 3d electrons.

The Weiss constant calculated from the fit of the paramagnetic data for $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ is small for both orientations; θ is 7.5 K for $H_{//c}$ and -4.4 K for $H_{\perp c}$. The small magnitude indicates magnetic coupling interactions between Pr^{3+} ions are weak; the opposing signs point to possible competing ferromagnetic and antiferromagnetic interactions, as would be expected for a complex structure featuring over 10 independent rare earth sites. This competition may also be the source of the very slight splitting of FC and ZFC data seen for both crystal orientations. FC/ZFC splitting may be caused by disorder or magnetic frustration leading to spin-glass formation.

The magnetization data shown in Figure 5c shed further light on this question. Above the ordering temperature, the

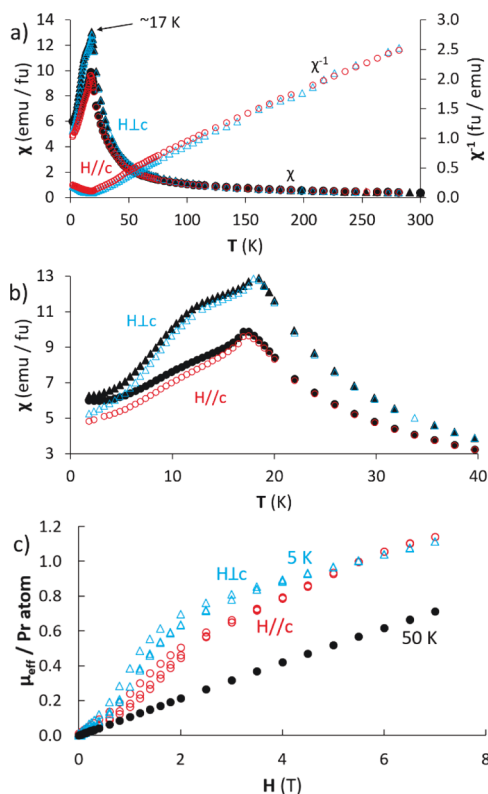


Figure 5. Magnetic susceptibility data for $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$. (a) Temperature dependence data under a field of 500 G applied either parallel (circles) or perpendicular (triangles) to the c -axis. FC data are indicated by closed black markers, and zero-field data are indicated by open colored markers. (b) Detail of temperature-dependent data shows divergence of FC and ZFC curves below 17 K. (c) Magnetization data for both orientations collected at 5 K, compared to magnetization in the paramagnetic state (at 50 K; black curve).

magnetization has the expected linear dependence on field for the paramagnetic state (50 K data). Below the ordering temperature, the data (collected at 5 K) are more complex. A larger net magnetization is seen when the crystal is oriented with the c -axis perpendicular to the applied field; this indicates a preference for the moments to align in the ab -plane. This is in agreement with the temperature dependence data (Figure 5a) which shows the moment at the Néel temperature ($T_N = 17$ K) is greater when the crystal is oriented so that the magnetic field is perpendicular to the c -axis. The magnetization in both orientations shows very small hysteresis at zero field, increasing at intermediate fields (5000–20 000 G), and then converging and approaching but not reaching saturation at higher applied fields. This is likely indicative of net antiferromagnetic coupling between the many Pr^{3+} sites leading to a complex canted antiferromagnetic ordering at low fields, and a metamagnetic transition to a differently ordered state at higher fields.

Magnetic susceptibility data for the cubic phase $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ were collected on a collection of randomly oriented crystals under an applied field of 500 G. Figure 6 shows the phase behaves paramagnetically at all measured temperatures. A slight downturn in susceptibility and divergence of the FC and ZFC curves starting at 3 K suggests a magnetic transition is occurring below the lower limit of the measurable temperature range. Fitting the inverse susceptibility curve above 100 K to the Curie–Weiss law yields a magnetic

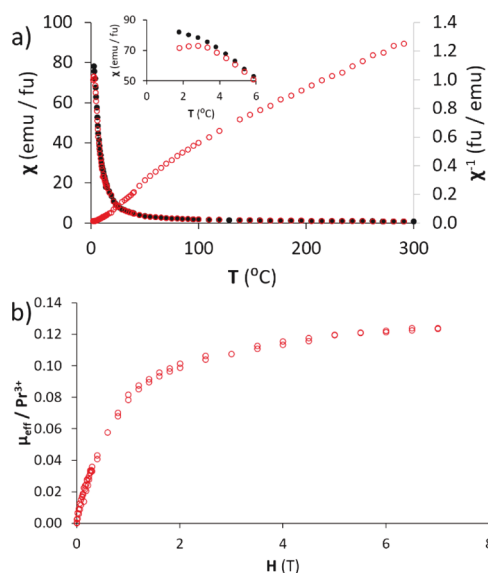


Figure 6. Magnetic susceptibility data for $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$. (a) Temperature dependence data under an applied field of 500 G. FC data are indicated by closed black dots, and zero-field data are indicated by open colored dots. Inverse susceptibility curves are plotted from ZFC data. The inset shows low-temperature splitting between FC and ZFC curves. (b) Magnetization data for $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$. Field-dependent data taken at 2 K.

moment per Pr^{3+} cation of $5.13 \mu_{\text{B}}$. The significantly larger value relative to that of individual free Pr^{3+} cations indicates contributions from the magnetic moment of iron atoms in the Fe_4C_6 clusters, which are within bonding distance of one another. The exact contribution of the iron atoms to the bulk magnetism is unclear without a neutron diffraction study of the magnetic structure. The large negative Weiss constant ($\theta = -58$ K) indicates strong antiferromagnetic interactions are present, which may contribute to the deviation from linearity of the inverse susceptibility curve below 100 K. However, this deviation is likely dominated by crystal field splitting of the Pr^{3+} 4f states. As was observed for the parent structure $\text{La}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$, this material may likewise be undergoing a spin-glass transition. Field dependence data were collected at 2 K; the low moment and lack of hysteresis indicate the compound is likely still in a paramagnetic state at this temperature. However, a saturation at higher fields shows the sensitivity of this state to external fields; this also points to a possible transition occurring at lower temperatures.

Electronic Structure Calculations. DOS calculations were carried out on two ordered model compounds for $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$; both models assume full occupancy of the $\text{Pr}(10)$ site. The $\text{La}_{63}\text{Fe}_{22}\text{Si}_{15}\text{C}_{32}$ model assumes full occupancy of the $\text{X}(4)$ site by Fe; the $\text{La}_{63}\text{Fe}_{20}\text{Si}_{17}\text{C}_{32}$ model assumes it is occupied by silicon. The DOS diagrams for both models are shown in Figure 7. Both exhibit a pseudogap slightly beneath the calculated Fermi level; a pseudogap at E_{F} is a stabilizing feature in intermetallics. In the Fe-rich model, the pseudogap is found at -0.127 eV; in the Si-rich model, it is found at -0.184 eV. The actual position of the gap will depend on the mixed Fe/Si site occupancy and the partial occupancy of the $\text{Pr}(10)$ site, both of which may occur in order to optimize the valence electron count to position the Fermi level in the pseudogap.³³

The iron and carbon states corresponding to the iron carbide framework are found well below the Fermi level for

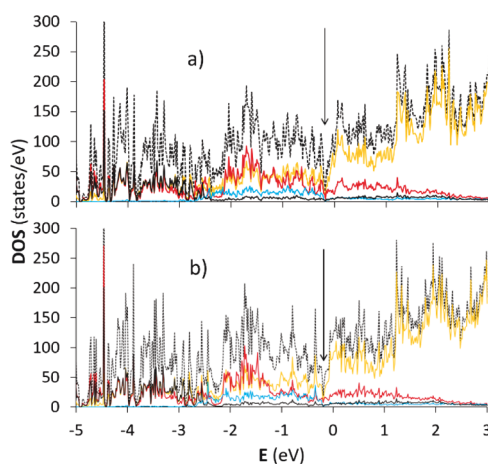


Figure 7. DOS data for the (a) Fe-rich $\text{La}_{63}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ model and (b) Si-rich $\text{La}_{63}\text{Fe}_{22}\text{Si}_{15}\text{C}_{32}$ model; the Fermi level is at 0 eV. In both plots, C states are represented in black, Si in blue, Fe in red, and La in yellow, with total DOS rendered in a black dashed line. The arrows highlight the pseudogaps just below the Fermi level.

both models, as narrow bands in the -2.5 to -5 eV range, indicating the electrons are localized. Interactions between iron d-states and surrounding La atoms are indicated by bands in the -1 to -2 eV range. The silicon states (and contributions from surrounding La atoms) are found in a broad energy range from 0 to 2.5 eV below E_{F} . La atoms make the dominant contributions at and above the Fermi level, indicating the bulk of the metallic conductivity will occur through the La/Si network.

Results of DOS calculations on the $\text{La}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ phase are shown in Figure 8. For this ordered compound, the Fermi energy lies inside a well-defined pseudogap, indicating the valence electron count is optimized. As was the case for the tetragonal phase, states derived from silicon and lanthanum orbitals dominate near the Fermi level, whereas the carbide

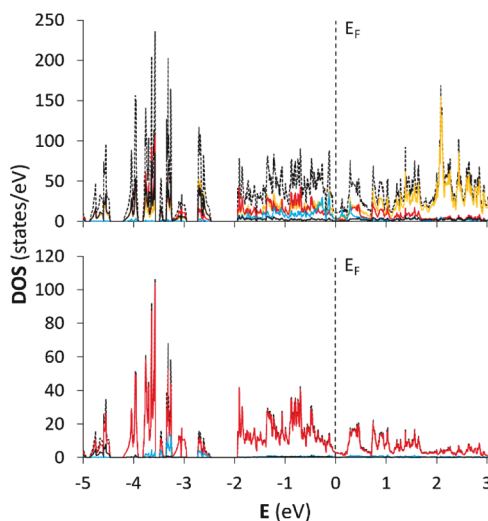


Figure 8. DOS stack plot showing results for $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$, with contributions per atom shown at the top and Fe contributions displayed at the bottom. In the top plot, C states are represented in black, Si in blue, Fe in red, and La in yellow, with total DOS rendered in a black dashed line. Fe d orbitals are shown in the bottom plot in red, p and s orbitals in blue and black, respectively, with full iron DOS shown with a dashed black line.

states lie well below it in the -2.5 to -5.1 eV region where they interact strongly with iron d-states. Additional Fe d states bracket the Fermi level. The lack of iron states at E_F is notable; transition-metal magnetism in intermetallics is typically associated with a d-orbital peak at the Fermi level which induces spin polarization and a resulting itinerant magnetic moment.³⁴ This indicates that $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ is not acting as an itinerant magnet and the observed iron moments derive instead from a different mechanism.

CONCLUSIONS

Rare earth/transition-metal mixed fluxes readily dissolve carbon, promoting the formation of novel intermetallic carbides. Reactions of carbon with iron and silicon in Pr/Ni melts form $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ and $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ -phases that exhibit similar stoichiometric ratios and share similar bonding motifs, particularly in their rare earth-main group element sublattices. These similarities and existence as competing products suggest that the tetragonal $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ phase is a kinetically stabilized intermediate that might convert to the more thermodynamically stable cubic product during the flux reaction. Competition between structurally related intermetallics has been observed in several metal flux systems; in situ studies (such as calorimetry measurements or variable temperature powder X-ray diffraction data collected on reactions as they cool) will be necessary to explore this possibility.³⁵ The $\text{La}_{21}\text{Fe}_8\text{Sn}_7\text{C}_{12}$ structure type accommodates a wide range of main group elements, but the $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$ type has been found only in the systems Ce/Fe/Al/C and Pr/Fe/M/C (M = Si, P, S) thus far.²⁸ The main group element reactant may determine the product formed because of a size effect, with the formation and stability of $\text{M}@\text{R}_n$ clusters dependent on the relative sizes of the main group atom and surrounding rare earth atoms. Reactions are planned to see if larger rare earth elements will accommodate progressively larger main group elements into this tetragonal $\text{Ln}_{62}\text{Fe}_{21}\text{M}_{16}\text{C}_{32}$ structure type. The variation in iron connectivity in the two structures is the likely source of their differences in magnetic behavior, with iron not having a moment in $\text{Pr}_{62}\text{Fe}_{21}\text{Si}_{16}\text{C}_{32}$, whereas the iron in the Fe_4C_6 clusters of $\text{Pr}_{21}\text{Fe}_8\text{Si}_7\text{C}_{12}$ does contribute to its magnetic moment. Mössbauer spectroscopy and/or neutron diffraction studies are needed to determine the nature of the iron moment in this compound.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.inorgchem.8b02741](https://doi.org/10.1021/acs.inorgchem.8b02741).

Atomic positions and thermal parameters for Pr/Fe/Si/C phases. Additional crystallographic data deposited with the CCDC as CIF files (PDF)

Accession Codes

CCDC [1869907–1869911](https://doi.org/10.1021/acs.inorgchem.8b02741) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: latturner@chem.fsu.edu.

ORCID

Susan E. Latturner: [0000-0002-6146-5333](https://orcid.org/0000-0002-6146-5333)

Notes

The authors declare no competing financial interest.

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