The Crystal Structure, Electronic, and Magnetic Properties of NaPd₃Ge₂

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Abstract

Crystals of NaPd₃X₂, (X = Si, Ge, Sn) were synthesized and their crystal structures investigated by single crystal x-ray diffraction. The previously reported structures of NaPd₃Si₂ and NaPd₃Sn₂ were confirmed. NaPd₃Ge₂ was found to have a different unit cell from that originally reported; therefore the structure was solved. It is an orthorhombically distorted version of the hexagonal CeCo₃Be₂-type structure, in space group *Imma*, with cell parameters $a = 7.244(1) \text{ \AA}$, $b = 9.938(1) \text{ \AA}$, $c = 5.767(2) \text{ \AA}$. The originally reported cell is explained through triple twinning of the true cell. The structure of NaPd₃Ge₂ fits the trend of decreasing X-X dimerization as a function of increasing period from Si – Sn. All three compounds are metals showing weak diamagnetism with increasing resistivity from NaPd₃Si₂ – NaPd₃Sn₂; no superconductivity is observed down to 2 Kelvin.

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Introduction

The CaCu_5 structure type (space group $P6/mmm$) has been widely studied, as several hundred compounds crystallize in this structure type and its derivatives^{1,2}. A diverse array of structures can be derived from the hexagonal, channel-forming structure of CaCu_5 . Related structures include the BaZn_5 structure type³ (containing zig-zag chains of cations) and the $\text{A}_x\text{T}_4\text{M}_4$ structure type⁴ ($\text{A} = \text{Na, K, Rb, Cs}$; $\text{T} = \text{Pd, Pt, Au}$; $\text{M} = \text{Si, Ga, Ge, In, Sn}$) which also contains channels of cations. A common set of derivative phases with the formula RT_xM_y is found where R is a rare earth, alkali/alkaline earth or Sc, Zr, Hf, U or Th ; T is a late transition element; and M is a main group element from groups 13 or 14. Most commonly $x + y = 5$, like in the RT_3M_2 set of compounds. Of particular interest have been compounds in the $P6/mmm$ CeCo_3B_2 structure type, which is related to CaCu_5 by substituting boron on the 2c position, one of two crystallographically distinct Cu sites in CaCu_5 ⁵. This creates two layers in the a - b plane of the compound: a Kagome net layer consisting of the Co alone, and a hexagonal net layer comprised of boron hexagons in a honeycomb lattice with Ce occupying the center of each hexagon. These layers are stacked so that the Ce sits above and below the center of the Kagome net layer, forming a Ce chain along the c -axis inside a channel formed by B. A few borides and silicides in the CeCo_3B_2 structure type are known to superconduct: ThRu_3B_2 , LuOs_3B_2 , LaRh_3B_2 , RlR_3B_2 ($\text{R} = \text{La, Th}$), and RRu_3Si_2 ($\text{R} = \text{Y, Th and La}$) being examples^{6,7}.

There are five common distortions of the RT_3M_2 , CeCo_3B_2 structure type: the monoclinic ErIr_3B_2 type⁸, the orthorhombic ErRh_3Si_2 type⁵, the rhombohedral ZrCo_3B_2 type⁹, the hexagonal LaRu_3Si_2 type¹⁰, and the hexagonal URu_3B_2 type¹¹. ErIr_3B_2 has a weak monoclinic distortion of the ideal structure, driven by its boron sublattice. ErRh_3Si_2 and ZrCo_3B_2 both show the formation of dimers in the honeycomb net (Si-Si and B-B dimers, respectively), but the locations of the Er and Zr atoms with respect to the honeycomb nets are different, resulting in orthorhombic versus rhombohedral distortions. In the LaRu_3Si_2 and URu_3B_2 structure types, in contrast, the change in symmetry is driven by a distortion in the transition element sub lattice.

When comparing the isoelectronic compounds NaPd_3Si_2 , NaPd_3Ge_2 , and NaPd_3Sn_2 it appears that the deviation from hexagonal symmetry due to M-M dimerization in the honeycomb sublattice is restored upon increasing the M element size. It was previously reported that NaPd_3Si_2 (SG # 44 $I2mm$) crystallizes in the orthorhombic ErRh_3Si_2 structure type and NaPd_3Sn_2 crystallizes in the CeCo_3B_2 structure type⁴. NaPd_3Ge_2 , the intermediate compound, was suggested to display a large volume orthorhombic unit cell with a volume 16 times that of a hexagonal CeCo_3B_2 -type cell, implying the presence of a

complex structural distortion, but a structural solution was never successfully completed⁴. Here we report the single crystal structural determination of NaPd₃Ge₂. We find that it actually crystallizes in the ErRh₃Si₂ structure type, and displays Ge-Ge dimerization^{12, 13} in the same pattern displayed by the silicide. The crystals are triply twinned, in a geometry that can lead to the belief that the compound has the larger, more complex orthorhombic cell previously hypothesized.

Experimental

Samples of NaPd₃Sn₂, NaPd₃Ge₂, and NaPd₃Si₂ were prepared via solid state reaction from Na metal, Pd (Alfa-Aesar 99.99% 100 mesh powder), and purified Ge or Sn ingot (Alfa-Aesar, 99.99%) or Si powder (Alfa-Aesar 99.99%). The elements were added to a tantalum tube in a 4:3:2 ratio. The tube was sealed under an argon atmosphere and then in turn sealed in an evacuated quartz tube. The Ge and Si samples were heated at the rate of one degree per minute to 600 °C and held there for one day before being heated to 1000 °C for 1 hour and then annealing at 700 °C for two days. The Sn sample was heated to 600 °C and held there for four days. The samples were then washed with water to dissolve the excess sodium and single crystals suitable for single crystal x-ray diffraction (SXRD) were removed. To make samples for resistivity and susceptibility measurements, the products obtained after the synthesis and washing procedure were pressed into pellets, resealed in an evacuated quartz tube, and fired at 500 °C for two days, after which they were cooled at 3 °C/min to room temperature. Phase purity for these samples was checked by powder X-ray diffraction (PXRD); no discernable impurity peaks were visible. The crystal structures for the three compounds were determined by SXRD. Data was collected on a Bruker D8 VENTURE using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) at 100 K and on a Bruker APEX II using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 100 K and 296 K. Frame width was 0.5° and exposure time was 10 seconds and 30 seconds, respectively, with a detector distance of 40 mm and 60 mm. Unit cell refinements and data integration were performed with Bruker APEX II and Bruker SAINT software^{14,15}. The crystal structures were refined using the full-matrix least-squares method on F^2 , implemented through SHELXTL-2013¹⁶ and WinGX¹⁷.

Magnetic susceptibility (χ) and electrical resistivity (ρ) measurements were performed with a Quantum Design Physical Property Measurement System (PPMS) using the ACMS and Resistivity options. Magnetic susceptibility was measured as a function of temperature in the 10 – 300 K range at an applied field of 1 Tesla; the measured magnetization (M) was linear in applied field (H) to fields higher than 1 Tesla and therefore χ was taken as M/H . The resistivity was also measured in the same

temperature range on a sample of approximate size 1.2 mm x 1.2 mm x 0.8 mm. Platinum wires were attached in four-point configurations using room-temperature-cured silver paint.

Results and Discussion

Single Crystal X-ray Diffraction

NaPd₃Si₂ and NaPd₃Ge₂ both formed rod-like crystals, while NaPd₃Sn₂ formed hexagonal plates. SXRD measurements of all species were done at 300 K as well as 100 K in order to look for low temperature structural phase changes such as localization of the Na in NaPd₃Sn₂ or further structural distortions in NaPd₃Si₂ or NaPd₃Ge₂. NaPd₃Si₂ confirmed that the previously reported structure exists down to 100 K. Similarly, NaPd₃Sn₂, also measured to 100 K, was confirmed to remain in the previously reported hexagonal cell on cooling. A specimen of NaPd₃Ge₂, of approximate dimensions 0.011 mm x 0.013 mm x 0.192 mm, was analyzed and the structure solved. A total of 1549 frames were collected over a total exposure time of 4.30 hours with Cu K α radiation. Initially, the arrangement of spots in the reciprocal lattice seemed to confirm the large previously reported orthorhombic cell, however when integrating the data it became evident that there was a large number of missing reflections. Figure 1a shows the reciprocal lattice precession image of the 3kl plane of the primary domain. No space group could be assigned to account for all of the missing reflections in a systematic fashion. Considering the chemical similarity of Si and Ge, it was hypothesized that NaPd₃Ge₂ could be crystallizing in the ErRh₃Si₂ structure but with systematic twinning, because a single domain of an ErRh₃Si₂-type cell could not account for the spacing of reflections seen. An orthorhombic cell slightly larger than the NaPd₃Si₂ cell was approximated using the size difference between Si and Ge and the software CELL_NOW¹⁸ was used to identify and isolate the twin domains. Through performing this analysis on several crystals, it was found that NaPd₃Ge₂ consistently crystallizes in a triply twinned fashion with secondary and tertiary domains related to the primary domain by rotating 180° around the [0 1 1] axis and [0 -1/3 1] axis respectively. The inset of Figure 1 shows the [301] reflections for the three domains as well as the d-spacing of the 301 planes, and Figure 1b shows the same reciprocal lattice precession image with the reflections from three twin domains outlined, clearly explaining every peak. With these twin laws, analysis of the data using CELL_NOW and the software TWINABS¹⁹, yielded a total of 2454 single and composite observations with 334 independent reflections to a maximum θ angle of 68.06°, 0.83 Å resolution, average redundancy 1.000, completeness = 99.5%, R_{int} = 8.12% and 329 reflections (98.50%) greater than $2\sigma(F^2)$. The twinning can also be described as a systematic rotation of the domains around

the c axis of a hexagonal cell similar to NaPd_3Sn_2 . This is likely the result of symmetry breaking during cooling of a high temperature hexagonal cell. Quenching from high temperature may be able to kinetically trap this phase. The final cell constants of $a = 7.244(1) \text{ \AA}$, $b = 9.938(1) \text{ \AA}$, $c = 5.767(2) \text{ \AA}$, volume = $415.14(12) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 1395 reflections above $20 \sigma(I)$ with $17.77^\circ < 2\theta < 136.0^\circ$ and is consistent with the parameters found by PXRD. Data were corrected for absorption effects using TWINABS and the ratio of minimum to maximum apparent transmission was 0.499. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.0170 and 0.3550. The structure was solved with SHELXTL using HKLF4 data for the first domain only, and then refined with the combined data in the HKLF5 format. Systematic absences of the $h + k + l \neq 2n$ and $hk0$ $h, k \neq 2n$ reflections lead to the possible space groups $Ima2$, $Im2a$ and $Imma$. The full-matrix refinement was carried out in $Imma$ and the refinement details and structural parameters of NaPd_3Ge_2 are summarized in Table 1. The structure was solved and the space group known before the HKLF5 file was produced. TWINABS removed the systematic absence violations due to the other domains. The twin domains were calculated to contribute in a 60.944/34.440/4.616 ratio.

Crystal Structure and Physical Properties

Table 2 summarizes the structural parameters, anisotropic thermal parameters and relevant atom-atom distances in NaPd_3Ge_2 , and Figure 2a shows the structure as well as a comparison between the puckered channels in NaPd_3Ge_2 and the ideal channels in NaPd_3Sn_2 . NaPd_3Ge_2 crystallizes in the ErRh_3Si_2 structure, a distortion of the CeCo_3B_2 structure type which belongs to the RT_3M_2 structures that are derivatives of the CaCu_5 structure type. It has pseudo-hexagonal channels, running along the a axis, that are formed by stacking slightly puckered Kagome net layers of Pd (formed in the bc plane) with distorted honeycomb layers of Ge (also formed in the bc plane) that also contain the Na (Figure 2b). The Ge atoms are not located on the vertices of an ideal honeycomb sublattice, however, due to the formation of Ge-Ge dimers which distort the Ge-Ge hexagons and cause the Na atoms to localize off center in the layer, closer to the Ge dimers than the undimerized Ge atoms in the hexagon, as is illustrated in Figure 3a. By stacking the layers so that the Na sits above the hole in the Pd Kagome layer, zig-zag sodium chains are created. The Ge-Ge dimers also cause a puckering of the Pd-Ge channels. There are two distinct Pd sites. In one, the Pd is surrounded by four Ge atoms in a coordination that is deformed into a trapezoid (Figure 3b) and in the other, the Pd is in a nearly square planar coordination with Ge (Figure 3c). The Pd(2) atoms have an elongated ellipsoid^{20, 21} toward each other that is likely due to a positional disorder along the a -axis. As can be seen in Figure 3b, the Pd-Ge trapezoid has two

acute angles and two obtuse angles as well as two short Pd-Ge bonds and two long PdGe bonds. This same motif is seen in NaPd_3Si_2 , with the notable difference that the M-M separation in the dimer is smaller in the Si case (Si dimer = $2.587(5) \text{ \AA}$ ⁸, Ge dimer = $2.675(2) \text{ \AA}$). The Si-Si dimerization in NaPd_3Si_2 causes a greater off-center displacement of the Na and distortion of the Pd sublattice than is seen in the Ge case. NaPd_3Sn_2 , on the other hand, crystallizes in the CeCo_3B_2 hexagonal structure type. The lack of dimers allows both Pd and Sn atoms to occupy the ideal sites in the Kagome and hexagonal layers, respectively. The Na atoms sit in the center of the Na/Sn hexagons, but are delocalized along the *c*-axis. As expected, the dimer weakens from NaPd_3Si_2 to NaPd_3Ge_2 until in NaPd_3Sn_2 , no dimers are present. The zig-zag aspect of the Na chain is dependent on the puckering of the channels which is, in turn, dependent on the extent of the dimerization. As one proceeds from the Si to the Ge to the Sn variant, the zig-zag chain straightens out when the dimers break and the ideal hexagonal symmetry is restored. The breaking of the dimers may also result in a different effective charge per Pd atom. Electronic structure calculations would be of interest to determine whether this is the case.

All three compounds exhibit diamagnetic behavior (Figure 4 inset) with χ on the order 10^{-6} emu/mol. As can be seen from Figure 4, they are all also metallic conductors down to 2 K. NaPd_3Si_2 appears to be the most metallic out of the group, while NaPd_3Sn_2 is the least, by an order of magnitude. Due to the polycrystalline nature of the samples, however, the magnitudes of the resistivities cannot be taken at face value; further study on single crystals would be required to specify the temperature dependent behavior of the resistivity in detail.

Conclusion:

Single crystal x-ray diffraction studies of NaPd_3X_2 , (*X* = Si, Ge, Sn) show that NaPd_3Si_2 and NaPd_3Sn_2 both have the structures previously reported⁴; no dimerization of the Sn honeycomb is found down to 100 K. NaPd_3Ge_2 was found to consistently form triply twinned crystals; this gave rise to the previously reported unit cell. The structure of NaPd_3Ge_2 was solved and it is found to crystallize in the ErRh_3Si_2 structure, where hexagonal channels, running along the *a* axis, are formed by stacking Kagome net layers of Pd (formed in the *bc* plane) with hexagonal layers of Ge and Na. Ge dimers cause the channels to pucker and the sodium sits off-center inside the channel resulting in a zig-zag chain. All three compounds are found to be diamagnetic metals with increasing resistivity from NaPd_3Si_2 through to NaPd_3Sn_2 and no superconductivity is seen down to 2 K. In NaPd_3Sn_2 , the sodium atoms are disordered along the *a* axis, implying weakly bound Na atoms which may be able to be de-intercalated.

Future work that investigates the use of a strong nucleophile to pull Na out of the structure of the Sn variant (where the tunnels are more open) in order to change the electron count of the compound, may be of interest.

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Table 1: Single crystal structure determination for NaPd₃Ge₂, experimental data taken at 100 K.

Phase	NaPd ₃ Ge ₂
Symmetry	Orthorhombic, <i>Imma</i> (No. 74)
Cell Parameters (Å)	a = 7.244(1), b = 9.938(1), c = 5.767(2) $\alpha = \beta = \gamma = 90^\circ$
Wavelength (Å)	Cu K α - 1.54178
V (Å ³)	415.14(12)
Z	4
Calculated Density (g cm ⁻³)	7.798
Formula Weight (g mol ⁻¹)	487.37
Absorption Coefficient (mm ⁻¹)	118.631
Observations	2454
F ₀₀₀	852
Independent/Observed Reflections	334 / 329
Data/Restraints/Parameters	334 / 6 / 23
Difference e- density (e/ Å ³)	+1.172 to -1.360
R ₁ (all reflections)	0.0228
R ₁ Fo > 2 σ (Fo))	0.0224
wR ₂	0.0573
R _{int} /R(σ)	0.0812/0.0192
GooF	1.190

Table 2a: Refined structural parameters and anisotropic thermal parameters for NaPd₃Ge₂ at 100 K.

NaPd ₃ Ge ₂						
Atom Type	Label	Wyckoff	x	y	z	S.O.F.
Pd	Pd1	8f	0.7975(1)	½	½	1
Pd	Pd2	4c	¾	¾	¾	1
Ge	Ge1	8h	0	0.9207(2)	0.8127(2)	1
Na	Na1	4e	0	¾	0.713(1)	1
Anisotropic Thermal Parameters [Å ²]						
Atom Type		U ₁₁	U ₂₂	U ₃₃	U ₁₃	U ₂₃
Pd1		0.0072(6)	0.0016(6)	0.0045(6)	0	0.0005(4)
Pd2		0.0223(8)	0.0013(9)	0.0057(8)	0.0003(2)	0
Ge1		0.0066(7)	0.011(1)	0.0073(8)	0	0.0030(7)
Na1		0.005(3)	0.007(4)	0.009(4)	0	0

Table 2b: Selected distances in NaPd₃Ge₂, at 100K.

Atom1	Atom2	Distance Å		Atom1	Atom2	Distance Å
Na1	Pd1	3.136(3)		Ge1	Pd1	2.455(1)
	Ge1	3.219(6)			Pd1	2.534(1)
	Ge1	3.323(2)			Ge1	2.675(2)
	Ge1	3.473(6)			Ge1	3.392(3)
	Na1	3.647(1)			Ge1	3.694(1)
	Pd1	3.682(3)				
				Pd2	Ge1	2.507(1)
Pd1	Pd1	2.934(1)			Na1	3.226(6)
	Pd1	2.964(1)			Na1	3.588(6)
	Pd2	2.893(1)			Pd2	3.622(1)

Figure Captions

Figure 1 (color online) – a: SXRD precession image of the 3kl plane in the reciprocal lattice of NaPd_3Ge_2 . Inset shows the 301 set of reflections from the three domains, white labels belonging to the primary domain, yellow bold labels from the secondary domain and green italicized labels from the tertiary domain. The d-spacing of the 301 planes is also shown. **b:** Separation of the lattice into the three domains. Reflections lying on the solid white lines (guides to the eye) belong to the primary domain, and reflections lying on the yellow and green dashed lines (also guides to the eye) are from the secondary and tertiary domains, respectively.

Figure 2 (color online) – a: Left: NaPd_3Ge_2 structure looking down the b -axis at the channel running along the a -axis with thermal ellipsoids shown. Right: NaPd_3Sn_2 ideal hexagonal channel with disordered Na shown. **b:** A projection down the [100] axis showing one layer of the Kagome Pd net and the distorted hexagonal Ge net forming channels with Na in the centers of the hexagons. In subsequent layers, the Pd net is stacked on top of itself while each Ge net is rotated 180 degrees about the [100] from the previous layer, creating distorted channels.

Figure 3 (color online) – a: Ge coordinating in hexagonal planes around Na, where the Na is the yellow atom near the center. Note the Na sits off the center position and closer to the Ge dimers than the other Ge atoms, resulting in the zig-zag chain formation when stacking the layers along the a -axis. **b:** Pd-Ge trapezoidal polyhedra propagating along the a -axis. Pd are the grey atoms, Ge are the purple atoms. In **a** and **b**, Ge dimers are shown with black, dashed double lines. **c:** Pd-Ge nearly square plane polyhedra also propagating along the a -axis.

Figure 4 (color online): Resistivity versus Temperature for NaPd_3Sn_2 , NaPd_3Ge_2 , and NaPd_3Si_2 . NaPd_3Sn_2 range follows the left vertical axis while NaPd_3Ge_2 , and NaPd_3Si_2 ranges follow the right vertical axis. All three show metallic behavior with the Si compound having the least absolute resistivity at 2 K and the Sn having the most. Inset shows the weak diamagnetic behavior of all three compounds.

Figure 1:

Figure 2:

Figure 3:

Figure 4: