Superconductivity and structural variation of the electron-correlated layer systems
\[ \text{Sr(Pd}_{1-x}T_x)_{2}\text{Ge}_2 \quad (T = \text{Co, Ni, Rh}; 0 \leq x \leq 1) \]

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(Received 12 July 2011; revised manuscript received 26 December 2011; published 31 January 2012)

Superconductivity variations deduced from the x-ray diffraction and the magnetic and heat-capacity measurements in the pseudoternary \( \text{Sr(Pd}_{1-x}T_x)_{2}\text{Ge}_2 \) layer system \( \text{[Pd}(4d^9), T = \text{Co}(3d^7), \text{Ni}(3d^8), \text{or RH}(4d^6)); 0 \leq x \leq 1 \) are reported. For the \( \text{BaFe}_{2}\text{As}_2 \)-type tetragonal structure, the degenerate \( nd^7 \) or \( nd^8 \) orbitals of transition metal \( T \) are split by \( c \)-axis squeezed \( T \text{Ge}_2 \) tetrahedral crystal field in the \( T \)-\text{Ge} layer. For the isoelectronic \( \text{Sr(Pd}_{1-x}\text{Ni}_x)_{2}\text{Ge}_2 \) system, the superconducting transition temperature \( T_c \) decreases monotonically from 3.12 K for 4d-band \( \text{SrPd}_2\text{Ge}_2 \) to 0.92 K for 3d-band \( \text{SrNi}_2\text{Ge}_2 \), where major contributions of conduction electrons are from the half filled dispersive three-dimensional (3D)-like upper-lying \( nd_{x^2-r^2} \) bands. For the \( \text{Sr(Pd}_{1-x}\text{Rh}_x)_{2}\text{Ge}_2 \) system, \( T_c \) decreases to 2.40 K with 25% of 4d \( \text{Rh} \) substitution. For the \( \text{Sr(Pd}_{1-x}\text{Co}_x)_{2}\text{Ge}_2 \) system, \( T_c \) decreases sharply to 2.58 K with only 3% of 3d \( \text{Co} \) substitution. No superconductivity is expected for \( \text{SrRh}_2\text{Ge}_2 \) and \( \text{SrCo}_2\text{Ge}_2 \) with lower density of states in \( d_{x^2-r^2} \) bands due to down shift of Fermi energy \( E_F \) by one less electron per transition metal. The lower \( T_c \) of the present electron-overdoped (\( nd^7 \) or \( nd^8 \)) compound is due to dispersive 3D-like \( nd_{x^2-r^2} \) conduction bands with weak electron correlation, in comparison with the less-electron-doped (\( 3d^8 \)) 22-K superconductor \( \text{BaFe}_{1.8}\text{Co}_{0.2}\text{As}_2 \) or the hole-doped (\( 3d^8 \)) 38-K superconductor \( \text{Sr}_{0.8}\text{K}_{0.2}\text{Fe}_2\text{As}_2 \), where electron contribution is from less dispersive 2D-like lower-lying \( 3d_{xy} \) conduction band with stronger electron correlation.

DOI: 10.1103/PhysRevB.85.024538

PACS number(s): 74.70.-b, 61.05.cp, 61.66.Fn, 74.62.Dh

I. INTRODUCTION

The recent discovery of high superconducting transition temperatures \( T_c \) up to 55 K in the electron-correlated layer system \( \text{LaFeAs(O}_{1-x}\text{F}_x) \) had generated profound interest in the superconducting FeAs-based systems.\(^{1} \)

For the \( \text{AFE}_{2}\text{As}_2 \) (122) \( (A = \text{Ca, Sr, or Ba}) \) layer system with the \( \text{ThCr}_2\text{Si}_2 \)-type body-centered-tetragonal (bct) structure and space group \( I4/mmm \), \((\text{FeAs})^{1-}\) layers are separated by \( A^{2+} \) layers. The parent compound \( \text{BaFe}_2\text{As}_2 \) is a poor metal with an antiferromagnetic spin-density wave (SDW) transition at \( T_N = 140 \) K. \( T_c \) up to 38 K were reported in the hole-doped \( (\text{Ba}_{0.6}\text{K}_{0.4})\text{Fe}_2\text{As}_2 \) and \( (\text{Sr}_{0.6}\text{K}_{0.4})\text{Fe}_2\text{As}_2 \), in which one \( 4s \) valence electron in \( K^{1+} \) substituted two \( 6s \) valence electrons in \( \text{A}^{2+} \),\(^{2,3} \) and \( T_c \) up to 22 K were reported by the electron-doped \( \text{BaFe}_{1.8}\text{Co}_{0.2}\text{As}_2 \), in which seven \( 3d \) valence electrons in \( \text{Co} \) substituted six \( 3d \) valence electrons in \( \text{Fe} \).\(^{4-6} \)

For \( \text{BaFe}_{1.8}\text{Co}_{0.2}\text{As}_2 \) superconductor with anomalous tetragonal \( c/a = 3.275 \) due to squeezed \( \text{FeAs}_4 \) tetrahedron along the \( c \) axis, major carriers are electrons from Hall effect measurement. The local-density approximation (LDA) band calculation indicates that \( 3d \) electron density of states (DOS) has a downward shift on \( \text{Co}-3d^7 \) bands with stronger \( \text{Co}-3d^7-\text{As}-4p \) hybridization. The LDA Fermi surface shows low dispersive two-dimensional (2D)-like \( d \) bands and \( \text{Co} \) affects the states forming heavy-hole-like bands at zone center, not on lighter electronlike bands around the zone boundary.\(^{4-6} \)

The \( \text{A(Fe}_{1-x}\text{Co}_x)_{2}\text{As}_2 \) pseudoternary phase diagram \( (A = \text{Ca, Sr, Ba}; 0 \leq x < 0.13) \) is similar to other high-\( T_c \) systems with a tetragonal to orthorhombic structural transition \( T_x \) before antiferromagnetic SDW transition \( T_N \). The electron correlation strength varies from strongly correlated regime to weakly correlated regime with increasing electron doping parameter \( x \).\(^{7-12} \)

Superconductivity was also discovered in the arsenic-free ternary germanide system \( \text{SrT}_{2}\text{Ge}_2 \) (\( T = \text{transition metals} \) with the same \( \text{BaFe}_2\text{As}_2 \)-type bct structure where \( (\text{PdGe})^{1-} \) layers are separated by \( \text{Sr}^{2+} \) layers.\(^{13-15} \) \( T_c \) up to 3.04 K was reported for \( \text{SrPd}_2\text{Ge}_2 \).\(^{15} \) Single-crystal \( \text{SrPd}_2\text{Ge}_2 \) synthesized by the metal flux method shows a lower \( T_c \) of 2.7 K with a moderate magnetic anisotropy.\(^{10} \) The LDA band-structure calculation for \( \text{SrT}_{2}\text{Ge}_2 \) \( (T = \text{Pd and Ni}) \) suggested higher dispersion energy bands across Fermi energy \( E_F \) with partial DOS contributions from \( T-3d \) and \( \text{Ge}-4p \).\(^{17} \) Superconductivity of \( \text{SrNi}_2\text{Ge}_2 \) with \( T_c = 0.92 \) K was reported recently by our group using low-temperature resistivity measurement.\(^{18} \)

In this paper, we try to answer two critical questions: (1) What is the variation of superconductivity with crystal and electronic structure in the electron-correlated layer system
Sr(Pd$_{1-x}$T$_x$)$_2$Ge$_2$ ($T =$ Co, Ni, Rh)? (2) What is the origin of higher-$T_c$ in the isostructural BaFe$_{1-x}$Co$_x$As$_2$ layer system?

II. EXPERIMENT

The ternary and pseudoternary Sr(T$_1$-$x$T$_x$)$_2$Ge$_2$ samples ($T', T = $ Co, Ni, Rh, or Pd; 0 $\leq$ x $\leq$ 1) were prepared by two-step arc melting under argon atmosphere. High-purity transition metals Co, Ni, Rh, and Pd (>99.9%) were arc melted with Ge (99.9999%) to form intermediate compound (T$_1$-$x$T$_x$)Ge$_2$, and then melted carefully with Sr metal (99.5%). Due to high vapor pressure of Sr at the melting temperature, extra Sr was added to compensate for the evaporation loss and to ensure the stoichiometric ratio of Sr:(T$_1$-$x$T$_x$):Ge = 1:2:2 to within 1%.

The x-ray powder-diffraction (XPD) data were collected by a Rigaku Rotaflex 18-kW rotating anode diffractometer with graphite monochromatized Cu-K$_\alpha$ radiation with a scanning step of 0.02° in the 2θ range 5°-100°.

The electrical resistivity was measured by a standard four-probe method in a He refrigerator from 0.4 to 300 K. The magnetic susceptibility and magnetization data were collected with a Quantum Design 1-T magnetic shielded MPMS$^2$ superconducting quantum interference device (SQUID) magnetometer from 2 to 300 K. The low-temperature heat-capacity superconductor was observed for Pd with eight 4$d$ electrons, which is similar to 122.4° for the isoelectronic Ni with eight 3$d$ electrons, but is greater than 118.2° for Co with seven 3$d$ electrons and 116.1° for Rh with seven 4$d$ electrons.

The five degenerate $nd$ orbitals were split into an up-lying $t_{2g}$ triplet and a lower-lying $e_g$ doublet in the undistorted tetrahedral crystal field with bond angle of 109.3°. In the $c$-axis squeezed $T$Ge$_4$ tetrahedral crystal field, the $t_{2g}$ triplet is further split into one up-lying doublet and one lower-lying $d_{xy}$ level. The $e_g$ doublet is split into $d_{xz}$ and $d_{yz}$ levels. The conductive bands are formed by $d_{xz}$, $d_{yz}$, and $d_{xy}$ orbitals with light electronlike bands from an up-lying $d_{xz}$ doublet and a heavy-hole-like band from a lower-lying $d_{xy}$ level. With eight $nd$ electrons in $T$ Ge and Pd, the $d_{xz}$ and $d_{yz}$ bands are close to half filled, with some hole pockets in the lower $d_{xz}$ band, and no Fermi surface is expected on lower-lying $d_{zy}$ and $d_{yz}$ bands. With seven $nd$ electrons in $T$Co and Rh and a down shift of Fermi energy $E_F$ by one less electron, the $d_{xz}$ and $d_{yz}$ bands are less than half filled, with some hole pockets in the lower $d_{xy}$ band.

III. RESULTS AND DISCUSSION

The ternary SrT$_2$Ge$_2$ compounds ($T =$ Co, Ni, Rh, Pd) crystallized with the BaFe$_2$As$_2$-type body-centered-tetragonal (bct) structure are shown in Fig. 1, with Sr at (2a):$\theta$(0, 0, 0), T at (4d):$(\frac{1}{2}$, $\frac{1}{2}$, 0), Ge at (4c):$\theta$(0, 0, z) of space group I4/mmm ($Z = 2$). The $T$Ge$_4$ layers are separated by Sr$^{2+}$ layers in this layer system. Within the layer, the $T$Ge$_4$ tetrahedron was squeezed along the $c$ axis, with different internal coordinates $z$ of Ge for each metal $T$ summarized in Table I.$^{13-17}$

The x-ray powder-diffraction patterns are shown collectively in Fig. 2 with the corresponding tetragonal lattice parameters summarized in Table I.

Lattice parameter $a$ and the $T$-$T$ bond length $d(T$-$T$) = $a/\sqrt{2}$ decrease with decreasing transition-metal $T$ sizes, from $d$(Pd-Pd) = 0.313 nm to $d$(Co-Co) = 0.288 nm, as shown in Table I. The long $T$-$T$ bond length indicates weak direct electron $T$-$T$ hopping within the $T$Ge layer.

An anomalous $c/a$ ratio increases from 2.286 for $T =$ Pd(4$d^8$) to 2.452 for Ni(3$d^8$), 2.558 for Rh(4$d^7$), and to 2.624 for Co(3$d^7$) due to the squeezed $T$Ge$_4$ tetrahedron along the $c$ axis, but is still smaller than $c/a$ = 1.2980 nm/0.3964 nm = 3.275 for the isostructural BaFe$_{1.8}$Co$_{0.2}$As$_2$ superconductor.$^{4,6}$

All bond angles $\theta$(Ge-$T$-Ge) in the squeezed tetrahedron along the $c$ axis of the pseudoternary systems Sr(Pd$_{1-x}$T$_x$)$_2$Ge$_2$ ($T =$ Co, Ni, Rh) are larger than 109.3° for unsqueezed ideal tetrahedron as shown in Fig. 3. A bond angle of 122.5° is observed for Pd with eight 4$d$ electrons, which is similar to 122.4° for the isoelectronic Ni with eight 3$d$ electrons, but is greater than 118.2° for Co with seven 3$d$ electrons and 116.1° for Rh with seven 4$d$ electrons.

TABLE I. Lattice parameters summarized from the x-ray powder-diffraction data of the tetragonal SrT$_2$Ge$_2$ system ($T =$ Pd, Ni, Rh, Co) with respective $z$ coordinates of Ge at (4e): $(0, 0, z)$.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$z$(Ge)</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
<th>$d$(T$T$) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>0.370</td>
<td>0.4402(4)</td>
<td>1.0104(10)</td>
<td>2.286</td>
</tr>
<tr>
<td>Ni</td>
<td>0.362</td>
<td>0.4181(4)</td>
<td>1.0251(10)</td>
<td>2.452</td>
</tr>
<tr>
<td>Rh</td>
<td>0.368</td>
<td>0.4193(4)</td>
<td>1.0724(10)</td>
<td>2.558</td>
</tr>
<tr>
<td>Co</td>
<td>0.364</td>
<td>0.4071(4)</td>
<td>1.0683(10)</td>
<td>2.624</td>
</tr>
</tbody>
</table>
FIG. 2. (Color online) X-ray powder-diffraction (XPD) patterns for the tetragonal Sr$_2$Ge$_2$ system (T = Co, Ni, Rh, Pd), arranged in increasing c/a ratio.

The T-Ge bond length $d(T$-Ge) = $\left[ a^2/4 + (z - 1/4)c^2 \right]^{1/2}$ as shown in the inset of Fig. 3 decreases with decreasing transition-metal T size, from 0.252 nm for Pd to 0.237 nm for Co. The short T-Ge bond length indicates strong hybridization between T-$nd$ and Ge-$4p$ orbitals, with delocalized, itinerant electron hopping through this channel.

The LDA band-structure calculation for Sr$_2$Ge$_2$ (T = Pd and Ni) suggests higher dispersion energy bands across Fermi energy $E_F$ with a multisheet Fermi surface and low total DOS at $E_F$ with partial DOS contributions from T-$3d$ and Ge-$4p$. However, a small but nonzero on-site Coulomb repulsion $U$ ($U \sim 0.5$ bandwidth $W$) is probably needed in the LDA + $U$ calculations for this electron-correlated system to get a more realistic band structure. The LDA calculation expects superconductivity in SrNi$_2$Ge$_2$. Indeed a superconducting transition temperature $T_c$ = 0.92 K was recently observed by our group. The temperature dependence of electrical resistivity ratio $\rho(T)/\rho(1$ K) of new superconductor SrNi$_2$Ge$_2$. Inset reveals a $T_c$ (onset) at 0.92 K.

FIG. 3. (Color online) Variation of bond angle $\theta$(Ge-T-Ge) for squeezed TGe$_4$ tetrahedron and bond length $d$(T-Ge) (inset) for pseudoternary systems Sr(Pd$_{1-x}$T$_x$)$_2$Ge$_2$ (T = Co, Ni, Rh).

FIG. 4. (Color online) Temperature dependence of electrical resistivity ratio $\rho(T)/\rho(1$ K) of new superconductor SrNi$_2$Ge$_2$. Inset shows a $T_c$ (onset) at 0.92 K.

FIG. 5. (Color online) Temperature dependence of molar heat capacity $C(T)$ for superconductor SrNi$_2$Ge$_2$. $C/T^2$ plot for zero applied field and $B_a = 7$ T are shown collectively in the inset. Normal-state heat capacity at $B_a = 7$ T can be fitted with the formula

$C_N(T) = \gamma T + A T^3$, with an electronic $\gamma = 1.55 \times 10^{-2}$ J/mol K$^2$ and a Debye temperature $\theta_D = 175$ K. The superconducting specific-heat jump $\Delta C/\gamma T_c$ of 1.2 is very close to the BCS value of 1.43. 

Anisotropic superconducting properties are expected for this layer system. Polycrystalline SrPd$_2$Ge$_2$ powder (grain size 1–10 μm) was aligned at room temperature in an alignment magnetic field of 0.9 T utilizing anisotropic paramagnetic magnetization due to the T-Ge layer structure. An easy electron correlation. The lower superconducting transition temperature of this electron-overdoped (nd$^8$) compound is probably due to more dispersive 3D-like 3$d_{xz,yz}$ conduction bands, as compared with the less-electron-doped (3d$^6$) 22-K superconductor BaFe$_{1.9}$Co$_{0.2}$As$_2$ or the hole-doped (3d$^5$) 38-K superconductor Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ with less dispersive 2D-like 3$d_{xz,yc}$ conduction band.

Figure 5 shows the low-temperature heat capacity $C(T)$ of the SrNi$_2$Ge$_2$ superconductor. A heat-capacity jump at $T_c = 0.78$ K was observed, which is slightly lower than $T_c$(zero) = 0.87 K measured by electrical resistivity. The $C/T^2$ vs $T^2$ plot for zero applied field and $B_a = 7$ T are shown collectively in the inset. Normal-state heat capacity at $B_a = 7$ T can be fitted with the formula

$C_N(T) = \gamma T + A T^3$, with an electronic $\gamma = 1.55 \times 10^{-2}$ J/mol K$^2$ and a Debye temperature $\theta_D = 175$ K. The superconducting specific-heat jump $\Delta C/\gamma T_c$ of 1.2 is very close to the BCS value of 1.43, which suggests a fully opened $s$-wave-type superconducting gap for this low-$T_c$ superconductor.

Anisotropic superconducting properties are expected for this layer system. Polycrystalline SrPd$_2$Ge$_2$ powder (grain size 1–10 μm) was aligned at room temperature in an alignment magnetic field of 0.9 T utilizing anisotropic paramagnetic magnetization due to the T-Ge layer structure. An easy superconducting transition temperature of this electron-overdoped (nd$^8$) compound is probably due to more dispersive 3D-like 3$d_{xz,yc}$ conduction bands, as compared with the less-electron-doped (3d$^6$) 22-K superconductor BaFe$_{1.9}$Co$_{0.2}$As$_2$ or the hole-doped (3d$^5$) 38-K superconductor Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ with less dispersive 2D-like 3$d_{xz,yc}$ conduction band.

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magnetization direction along the tetragonal basal plane through spin-orbit coupling related magnetocrystalline anisotropy was observed. The x-ray powder-diffraction (XPD) pattern for aligned powder in epoxy along the basal plane with enhanced (hk0) lines and along the c axis with enhanced (00l) lines are shown collectively in the inset of Fig. 6. Alignment was not complete probably due to intermediate alignment field strength of 0.9 T, insufficient curing time of 10 h, or simply intrinsic origin. Close to 85% alignment was achieved.

Anisotropic low-field field-cooled (FC) and zero-field-cooled (ZFC) magnetic susceptibility $\chi_{\text{anis}}(T)$ for aligned powder SrPd$_2$Ge$_2$ (grain size 1–10 $\mu$m) along the tetragonal c axis and basal plane are shown collectively in Fig. 6. With Pd-Ge bond length $d$(Pd-Ge) of 0.252 nm for this electron-overdoped compound, superconducting transition $T_c$ onset of 3.12 K was observed, which is slightly higher than the previously reported 3.04 K for bulk sample and 2.7 K for single crystal. At 2 K in applied field of 10 G smaller than lower critical field $B_{c1}(2 K)\sim 100$ G, a ZFC anisotropic molar susceptibility ratio $\chi_c$(ZFC)/$\chi_{\text{basal}}$(ZFC) = 9.5 cm$^3$ mol$^{-1}$/5.8 cm$^3$ mol$^{-1}$ ~ 1.6 at Meissner state was observed. A lower diamagnetic signal above 2.6 K is due to the small grain size where a 10-G field is already penetrated deeply into the grain.

The anisotropic initial diamagnetic magnetization curve and magnetic hysteresis loop $M(B_s)$ at $T = 2$ K < $T_c = 3.12$ K for aligned superconducting powder SrPd$_2$Ge$_2$ are shown collectively in Fig. 7. The peak field penetration into microcrystalline grain center (grain size 1–10 $\mu$m) $B_{\text{basal}}$(peak) is 56 G along the tetragonal basal plane and $B_c$(peak) is 44 G along the c axis. These peak values are slightly smaller than the average bulk $B_{c1}(2 K)\sim 100$ G due to the lack of grain-boundary pinning for small grain size and dispersed distribution of aligned microcrystalline in epoxy. The initial magnetization curve decrease to zero around 1 K is slightly higher than the upper critical field $B_{c2}(2 K)\sim 0.9$ K for the bulk sample. The small hysteresis loop shown in the inset of Fig. 7 reflects the low flux pinning behavior of the dispersive microcrystalline aligned powder.
bands while weaker $T_c$ suppression for Ni(3$d^8$) was attributed to the isoelectronic shift from the 4$d$ to 3$d$ band. The minor suppression in the latter system can be explained by similar band dispersion and Fermi surfaces between SrPd$_2$Ge$_2$ and SrNi$_2$Ge$_2$ compounds as indicated by band-structure calculations. No superconductivity is expected for SrRh$_2$Ge$_2$ and SrCo$_2$Ge$_2$ with lower DOS in $d$ bands due to the down shift of Fermi energy $E_F$ ($\sim 1$ eV) by one less electron per transition metal.

Figure 10 presents a variation of $T_c$ and bond lengths $d(T$-Ge) of the squeezed $T$Ge$_4$ tetrahedron in the $(T$Ge)$_4$$^-$ layer for pseudoternary SrPd$_{1-x}$Ni$_x$$_2$Ge$_2$ and Sr(Ni$_{1-x}$Co$_x$)$_2$Ge$_2$ systems. The $d(T$-T) bond length decreases from 0.31(Pd) to 0.29(Ni) nm, and enhanced direct hopping in the basal plane thus suppresses the $T_c$.

Compared with a smaller bond angle $\theta$(As-Fe$_{1.8}$Co$_{0.2}$-As) of 111.2$^\circ$ for 22-K superconductor BaFe$_{1.8}$Co$_{0.2}$As$_2$ with an average number 6.1 of 3$d$ electrons, the greater $\theta$ values of the present system indicates that a more 2D-like $d_{xy}$ band may contribute a higher $T_c$ for this compound.

The symmetry of superconductivity is probably a multiband s-wave symmetry and the mechanism of superconductivity for this low-$T_c$ system may require structural related anisotropic electron correlation with phonon mediation.

**IV. CONCLUSION**

The ternary and pseudoternary Sr(T$_{1-x}$T$_x$)$_2$Ge$_2$ system ($T'=\text{Co, Ni, Rh, or Pd}$) is an anisotropic tetragonal layer system where $nd$ orbitals of transition metal $T$ are split by the squeezed $T$Ge$_4$ tetrahedral crystal field. At the normal-metal state, the system is weakly electron correlated and close to the Fermi-liquid regime. The lower $T_c$ of the anisotropic electron-overdoped 3.12-K SrPd$_2$Ge$_2$ and 0.92-K SrNi$_2$Ge$_2$ compounds are the results of close to half filled dispersive 3D-like $nd_{xy,yz}$ conduction bands. No superconductivity is expected for SrRh$_2$Ge$_2$ and SrCo$_2$Ge$_2$ compounds with a lower density of states in these bands due to one less electron per transition metal.

**ACKNOWLEDGMENTS**

This work was supported by Grants No. NSC98-2112-M-007-013-MY3, No. NSC99-2811-M-007-095, and No. NSC99-2112-M-007-007 of the National Science Council of the Republic of China.