Superconductivity in Sr(Pd$_{1-x}$Ni$_x$)$_2$Ge$_2$

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Abstract. The systematic variations of lattice structure and superconducting transition temperature in Sr(Pd$_{1-x}$Ni$_x$)$_2$Ge$_2$ are reported. The X-ray diffraction patterns can be labeled by tetragonal $I4/mmm$ (no. 139) space group with only minor impurities, which indicates the substitution Ni into Pd sites is successful and formed pure phase. The tetragonal lattice parameter $a$ decreases and $c$ increases monotonically with Ni concentration $x$, while the unit cell volume decreases. A systematic, gradual change of superconducting transition temperature $T_c$ increases slightly to 3.2 K for very small Ni doping of $x \sim 0.1$ then slowly decreases to 2.1 K for $x = 0.5$. Further investigation for SrNi$_2$Ge$_2$ by low temperature resistivity indicated a $T_{c,mid}$ of 0.87 K suggesting that superconductivity exists through the whole Ni substitution levels.

1. Introduction

The appearance of superconductivity in iron-based pnictide compounds has attracted much attention, providing both a new aspect in understanding the physics of unconventional, non-BCS mechanism, superconductivity and a big new family of superconducting materials of fundamental and technological interest. Superconducting transition temperature $T_c = 26$ K was first reported in LaO$_{1-x}$F$_x$FeAs, later was raised to the highest $T_c$ in these materials $\sim 55$ K in SmFeAsO$_{1-x}$F$_x$ [1,2]. Oxygen-free compounds with the ThCr$_2$Si$_2$-type structure also exhibit superconductivity with a maximum $T_c \simeq 37$ K in (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$ (122 system) [3]. Because of the common structural element of Fe-As tetrahedral layer, these two systems are regarded as members of the same family and share a common mechanism of superconductivity. Due to the far better possibility to grow high quality and big crystals, a lot of research efforts were focused on the 122 systems for its superconducting properties and possible mechanisms. However, the importance of the 122-type compounds is not only for its easiness of high-quality crystals, but also for its wide variety of physical properties reported in a huge range of different compounds and compositions.

More recently the ThCr$_2$Si$_2$-type compound SrPd$_2$Ge$_2$ was reported to be superconducting with $T_c = 3.04$ K [4]. However, the reported property of the closely related compound SrNi$_2$Ge$_2$ was not superconducting down to 2 K with neither magnetic orderings [5]. To further explore the understandings of superconductivity in the 122-type structure, it is important whether superconductivity of SrPd$_2$Ge$_2$ is a singular existence or belonged to a series of superconductors with tunable physical variables related to the superconductivity. In this report, systematic

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Ni doped compounds \( \text{Sr}(\text{Pd}_{1-x}\text{Ni}_x)\text{Ge}_2 \) were synthesized and investigated for structural and superconducting properties. The existence of superconductivity and systematic variations of \( T_c \) with Ni concentration \( x \) were observed for the entire system.

2. Experimental

The intermetallic compounds \( \text{Sr}(\text{Pd}_{1-x}\text{Ni}_x)\text{Ge}_2 \) were prepared by two-step arc melting under Ar gas atmosphere on a water-cooled copper hearth. First the start materials having higher melting points, Pd wire (99.99%), Ni foil (99.99%) and Ge grains (99.9999%) were weighed by stoichiometric ratio and arc melted several times with intermediated turning over of the melted button. After that, Sr rock (99.5% pure) was added and carefully melted together with the previous button for several times to minimize the loss of Sr. The weight loss of the resultant samples were within a few percent. Structural analysis was performed by powder X-ray diffraction with a Rigaku Rotaflex 18-kW rotating anode diffractometer with graphite monochromatized Cu-K\( \alpha \) radiation in 2\( \theta \) range of 15\( ^\circ \)-65\( ^\circ \). The magnetic susceptibility measurements were performed by a QUANTUM DESIGN \( \mu \)-metal shielded 1-T MPMS\( _2 \) superconducting quantum interference device (SQUID) magnetometer at temperature range of 2-5 K. Low temperature Resistivity was done by standard four-probe technique in a \( ^3\)He refrigerator down to 0.4 K.

3. Results and discussion

The powder X-ray diffraction patterns of the as-melted samples \( \text{Sr}(\text{Pd}_{1-x}\text{Ni}_x)\text{Ge}_2 \) (0 \( \leq \) \( x \) \( \leq \) 0.5) were shown collectively in Figure 1 with each pattern shifted for clearance. The diffraction patterns can be well indexed by tetragonal ThCr\( _2 \)Si\( _2 \)-type structure as indicated in the figure. The minor impurities observed in some samples were marked by asterisks. The lattice constants were then obtained by least-square analysis on the indexed patterns which were in good agreement with the reported values of \( \text{SrPd}_2\text{Ge}_2 \) and \( \text{SrNi}_2\text{Ge}_2 \) [4,5]. The tetragonal \( a \)-axis contracted with the Ni doping monotonically from 0.4422 nm for \( x = 0 \) to 0.4292 nm for \( x = 0.5 \), then finally to 0.4178 nm for \( x = 1 \), while the \( c \)-axis increase from 1.0131 nm (\( x = 0 \)) through 1.0179 nm (\( x = 0.5 \)) to 1.0252 nm (\( x = 1 \)). The obtained unit cell volume shrinks almost linearly with the Ni concentration \( x \) from 0.19799 nm\(^3\) for \( x = 0 \) to 0.17922 nm\(^3\) for \( x = 1 \) which corresponds to \( V \sim 10\% \) decrease. On the contrary, the \( c/a \) values also increase nearly linearly from 2.29 (\( x = 0 \)) to 2.45 (\( x = 1 \)). The systematic variation of the tetragonal lattice constants \( a \) and \( c \) as well as only randomly observed minor impurities indicate that Ni can be substituted into the Pd-site of the \( \text{Sr}(\text{Pd}_{1-x}\text{Ni}_x)\text{Ge}_2 \) system without any solubility limit.

The low temperature, \( T \leq 4 \) K, molar magnetic susceptibility \( \chi_m(T) \) for \( \text{Sr}(\text{Pd}_{1-x}\text{Ni}_x)\text{Ge}_2 \) system with 10 G applied field \( B_a \) in zero-field-cooled (ZFC) mode was shown collectively in Figure 2. Meissner effect was observed clearly with a large diamagnetic signal indicates bulk

![Figure 1](image-url)
superconductivity of all compounds observed. The superconducting transition temperature $T_c$ of each Ni doping concentration was denoted by arrows at the onset of diamagnetic signal. A systematic change of $T_c$ with the Ni doping was observed. In the inset, low temperature ($T \leq 1.1$ K) resistance $R(T)$ of the $x = 1$ SrNi$_2$Ge$_2$ compound was shown. Superconductivity was confirmed by the rapid decrease of resistance below $T_{c,\text{onset}} = 0.915$ K which dropped to zero at $T_{c,0} = 0.845$ K with a transition mid-point and width of $T_{c,\text{mid}} = 0.87$ K and $\Delta T_c = 0.036$ K. The observation of $T_c$ varied through out the whole Ni substitution levels indicates the existence of superconductivity in all compounds of the system.

Figure 3 is the phase diagram of superconducting transition temperature as a function of Ni substitution level, $T_c$ vs $x$, for Sr(Pd$_{1-x}$Ni$_x$)$_2$Ge$_2$ system. As the Ni concentration increases, $T_c$ is first raised slightly from 3 K for SrPd$_2$Ge$_2$ to 3.2 K for $x = 0.1$, then gradually lowered down to 2.1 K for $x = 0.5$, SrPdNi$_2$Ge$_2$. By plotting the $T_c$ of SrNi$_2$Ge$_2$ into the phase diagram, it is more clear that the superconductivity exists through out the system and follows a systematic change. Combining information from both the structural, lattice parameters changed almost linearly, and superconducting $T_c$ has a slight maximum at $x = 0.1$, it is clearly indicated that Ni-doped Sr(Pd$_{1-x}$Ni$_x$)$_2$Ge$_2$ is a superconducting system whose $T_c$ is believed to be tuned by the electronic structure changed with $x$ due to structural changes and element substitution effects.

4. Conclusions

Compounds of Sr(Pd$_{1-x}$Ni$_x$)$_2$Ge$_2$ system were successfully synthesized in good quality. Systematic variations of tetragonal lattice parameters, $a$ and $c$, as well as superconducting $T_c$ with Ni concentration $x$ was reported. The finite $T_c$ was observed for the whole system which increases from 3 K ($x = 0$) to a slightly higher maximum 3.2 K ($x = 0.1$) then drops down monotonically to 0.87 K for $x = 1$.

Figure 2. Low temperature molar magnetic susceptibility $\chi_m(T)$ of Sr(Pd$_{1-x}$Ni$_x$)$_2$Ge$_2$ at 10 G applied field. The $T_c$’s were indicated by arrows at the onset of Meissner diamagnetic signal. Inset: The superconducting transition observed in SrNi$_2$Ge$_2$ by resistance.

Figure 3. Systematic variation of the superconducting transition temperature $T_c$ of the Sr(Pd$_{1-x}$Ni$_x$)$_2$Ge$_2$ as a function of Ni concentration $x$. The dashed line is draw as a guide to the eyes.
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