Superconductivity and the Effects of Pressure and Structure in Single Crystaline SrNi$_2$P$_2$

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Heat capacity, magnetic susceptibility, NMR, and resistivity of SrNi$_2$P$_2$ single crystals are presented, illustrating a purely structural transition at 325 K with no magnetism. Bulk superconductivity is found at 1.4 K. The magnitude of the transition temperature $T_c$ increases with the heat capacity data, the small upper critical field $H_{c2} = 390$ Oe, and Ginzburg-Landau parameter $\kappa = 2.1$ suggests a conventional fully gapped superconductor. With applied pressure a second structural phase transition occurs which results in an 8% reduction in the $c/a$ ratio of lattice parameters. We find that superconductivity persists into this high pressure phase, although the transition temperature is monotonically suppressed with increasing pressure. Comparison of these Ni-P data as well as layered Fe-As and Ni-As superconductor indicates that reduced dimensionality can be a mechanism for increasing the transition temperature.

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Introduction:

There have long been attempts to identify structure-property relations in superconducting materials that help in the identification of the pairing mechanism and the enhancement of the superconducting transition temperature. The discovery of superconductivity at 26K in LaFeAsO has stimulated much recent work in compounds containing T-Pn layers (T=transition metal, and Pn = pnictide). The highest transition temperatures to date are found in the tetragonal ZrCuSiAs structure (Pn = pnictide). The highest transition temperatures in the tetragonal ZrCuSiAs structure is generally 38 K in SmFeAs(O,F)$_2$, and a correlation has been identified between the As-Fe-As bond angle and $T_c$. Clearly, structural tuning can have a very dramatic effect on superconducting transition temperatures, and further structure-property relations are needed to help guide the discovery of higher transition temperatures.

Reasonably high transition temperatures also have been found in the ThCr$_2$Si$_2$ structure (i.e. 38 K in (Ba,K)Fe$_2$As$_2$). The ThCr$_2$Si$_2$ structure is stable for two different bonding configurations between the atoms in the Si position of neighboring Cr$_2$Si$_2$ planes. Either the atoms in the Si position are sufficiently far apart that they are in a non-bonding state, or they are close enough together that they are bonding (typical of single bond distances). Consequently, depending on the elements in the tetragonal ThCr$_2$Si$_2$ structure, one can induce an isostructural volume collapse with either substitution or pressure. We will refer to the bonding configuration as the "collapsed tetragonal" structure. Due to the increased bonding between layers, it is natural to anticipate that the collapsed tetragonal phase will be electronically more 3-dimensional (i.e. Fermi velocity ratio $v_F/v_2$ closer to 1) than the non-bonding configuration. With Fe$_2$As$_2$ planes, the ThCr$_2$Si$_2$ structure generally adopts a non-bonding configuration between As atoms from neighboring planes. One exception is that CaFe$_2$As$_2$ can be driven into the collapsed tetragonal state with pressure. Interestingly, while the homogeneous collapsed tetragonal state does not show signs of superconductivity down to 2 K, by using different pressure mediums a structurally inhomogeneous scenario is induced which possesses an onset of superconductivity at 13 K. This poses the question of what is the role of the collapsed tetragonal phase (and dimensionality in general) for superconductivity.

We attempt to shed light on this question with a study of SrNi$_2$P$_2$. At ambient pressure, SrNi$_2$P$_2$ crystallizes in the large tetragonal state above 325 K with an interlayer P-P distance of 3.120 Å corresponding to a non-bonding condition. Below 325 K, the system undergoes an orthorhombic distortion (Immm space group) with a buckling in the Ni$_2$P$_2$ planes causing the interlayer P-P distance to oscillate between 3.282 Å(non-bonding) and 2.452 Å(bonding). With NMR measurements we show that there is no magnetism associated with this transition. By applying pressure, the collapsed tetragonal state can be induced with slight pressure (4 kbar at room temperature). Here, we first identify that SrNi$_2$P$_2$ is a bulk superconductor at ambient pressure with $T_c = 1.4$ K. An analysis of the data is consistent with a fully gapped conventional superconductor. By applying pressure, we find that the transition temperature is suppressed by less than 50% upon entering the collapsed tetragonal state. Consequently, we conclude that the necessary conditions for superconductivity, namely the ability to create an attractive interaction which can over-
come the screened coulomb repulsion between two quasiparticles, can be satisfied in the "collapsed tetragonal" state to the transition metal pnictides in the ThCr$_2$Si$_2$ structure. Furthermore, by expanding the cell so as to increase the c/a ratio superconductivity is enhanced.

**Experimental:**

Large, plate-like single crystals of SrNi$_2$P$_2$ were grown in Sn flux following the general recipe described in ref. The starting materials in the ratio of Sr:Ni:P:Sn=1.3:2:2.3:16 were placed in an alumina crucible and sealed under vacuum in a quartz tube. The contents were then heated to 600 °C for 4 hours followed by 900 °C for 200 hours. Subsequently the charge was cooled to 650 °C at a rate of 3.5 °C/hour at which point the excess Sn was spun off with the aid of a centrifuge. Powder X-ray diffraction confirm that the large plate like crystals with typical dimensions 5 x 5 x 0.2 mm$^3$ were SrNi$_2$P$_2$.

Specific heat measurements were performed using an adiabatic relaxation technique in a Quantum Design PPMS. Resistance measurements were also performed in a Quantum Design PPMS using a Linear Research resistance bridge with an excitation current of 0.1 mA. Susceptibility measurements were performed in a Quantum Design MPMS with an applied field of 5 T. Results were in good agreement with data at 0.01 T, confirming that no ferromagnetic impurity contribution exists in the sample. $^{31}$P NMR was performed using a phase-coherent pulsed spectrometer. The external field was applied along the c-axis.

For pressure measurements, a crystal was mounted inside a Teflon cup within a hybrid BeCu/NiCrAl clamp-type pressure cell with silicon oil as the pressure transmitting medium. The cup also contained a small piece of Pb whose known pressure-dependent superconducting transition enabled a determination of the pressure within the cell at low temperatures where the superconductivity is measured.

**Results:**

The in-plane resistivity of SrNi$_2$P$_2$ is shown in figure and demonstrates a sharp first order anomaly with thermal hysteresis associated with the structural transition previously observed in X-ray diffraction measurements. Here we find the transition occurs at 325 K upon warming and 320 K upon cooling. The first order transition is further confirmed by magnetic susceptibility measurements shown in figure The susceptibility also shows the first order transition at 325 K (upon warming) and 322 K (upon cooling). Interestingly, the susceptibility in the high temperature phase is isotropic, but below the transition becomes anisotropic. While anisotropic g-factors can result in an anisotropic Pauli susceptibility it is surprising that only the low temperature phase shows this anisotropy.

To explore whether or not the susceptibility results could imply magnetic ordering or a changing magnetic moment coincident with the structural transition we performed $^{31}$P NMR above and below the transition (see fig-
The resistivity below the structural transition is characteristic of a good metal with a RRR (= $\rho(300\text{K})/\rho(4\text{K})$) of 40 and a residual resistivity of $1.8 \pm 0.2 \, \mu\Omega\text{cm}$. At 1.45 K the sample shows a sharp transition in resistivity which is consistent with bulk superconductivity as established by heat capacity measurements shown below. With an applied magnetic field the superconducting transition is rapidly suppressed indicating a very small upper critical field. In addition, with an applied magnetic field there is a slight upturn in the resistivity before the superconducting transition. A similar feature has been observed in other iron-based pnictide superconductors and is discussed in Ref. 12.

Specific heat data at low temperatures are shown in figure 3. A fit of the data (not shown) from 1.5 K to 10 K to $C/T = \gamma + \beta T^2 + \delta T^4$ gives $\gamma = 15 \, \text{mJ/mol K}^2$ and $\beta = 0.23 \, \text{mJ/mol K}^4$, which implies a Debye temperature $\Theta_D$ of 348 K. Using a zero-temperature susceptibility of $\chi_0 = (2\chi_{ab}(2K) + \chi_c(2K))/3 = 1.86 \, \text{emu/mol}$, we find a Wilson Ratio $R_W$ of 0.9 using the expression $R_W = 4\pi^2 \beta^2 / 3\gamma_B^2 (\chi_0 / \gamma)$.

Bulk superconductivity is established by specific heat measurements. By an equal area construction the specific heat gives a transition temperature of 1.415 K, consistent with the drop in resistivity. The fact that the low temperature specific heat gives a jump $\Delta C/\gamma T_c = 1.27$ confirms the bulk nature of superconductivity. From BCS theory we expect the specific heat to be given by the formula

$$C_{\text{BCS}}(T) = \frac{\hbar c}{2\pi^2} \frac{f}{\ln f + (1 - f) \ln (1 - f)}.$$

where $f = T/T_c$, $E = (c^2 + \Delta^2)^{1/2}$, $y = c/\Delta_0$, and $\Delta(T)/\Delta_0$ is taken from the tables of M"uhlschlegel.\textsuperscript{13} The specific heat curve, obtained by fixing $\gamma = 15 \, \text{mJ/mol K}^2$ from the high temperature fit, $T_c = 1.415$ K and $\Delta_0$ to the weak coupling BCS value $1.76 \, k_B T_c$, is shown by the solid black curve in fig. 3. Allowing the zero temperature gap value $\Delta_0$ to vary we obtain the dashed blue curve and find $\Delta_0 = 0.201 \, \text{meV} = 1.65 \, k_B T_c$. With the fitted curve to the specific heat, we can extract the condensation energy and equate it to the thermodynamic critical field giving $E_c = 185$ Oe. The reason that the best fit to the specific heat gives a value of $\Delta_0$ below the weak coupling value is uncertain, but may be caused by pair breaking impurities.\textsuperscript{19} We note that in several related superconductors the specific heat jump is also slightly smaller than the weak coupling BCS expectation of $\Delta C/\gamma T_c = 1.42$\textsuperscript{20,21,22,23,24}.

As mentioned above, the upper critical fields of SrNi$_2$P$_2$ are small. In figure 5 we plot the upper critical field deduced from the midpoint of the resistive transition as well as the midpoint of the specific heat curves. There is a slight anisotropy observed for the resistivity data. The upper critical field as determined by heat capacity is slightly lower, but surprisingly, shows no anisotropy. The slope of the upper critical field from heat capacity is $dH_{c2}/dT_c = -0.039$ T/K. This gives an upper critical field of 390 Oe using the WHH formula $H_{c2}(0) = -0.7 T_c dH_{c2}/dT_c$, and a Ginzburg-Landau coherence length $\xi_{GL} = 920$ Å from the expression $H_{c2}(0) = \Phi_0/2\pi\xi_{GL}^2$, where $\Phi_0 = 2.07 \times 10^{-7}$ Oe cm$^2$ is the flux quantum. From the relations $H_c/H_{c1} = H_{c2}/H_c = \sqrt{2\kappa} = \sqrt{2\lambda_{eff}}/\xi_{GL}$ we extract $\kappa = 2.1$, $H_{c1} = 88$ Oe, and $\lambda_{eff} = 1935$ Å.

To investigate the influence of the crystal structure on superconductivity, we applied pressure to SrNi$_2$P$_2$. At room temperature it is known that the orthorhombic structure transforms to a collapsed tetragonal structure at 4 kbar.\textsuperscript{8,9} Based on the pressure-temperature phase diagram for the structural collapse in CaFe$_2$As$_2$\textsuperscript{21} we anticipate that at lower temperatures the structural transition to the "collapsed tetragonal" phase in SrNi$_2$P$_2"}{\text{FIG. 3: $^{31}$P NMR of SrNi$_2$P$_2$ on cooling through the structural transition illustrating the absence of magnetism. The dotted line represents the resonance line in the absence of a Knight shift $K$.}}
will occur at pressures less than 4 kbar. The structural transformation results in a volume change of -3.9% and a -8% change in the c/a ratio. Low temperature resistivity is shown in figure 6b. There is an immediate discontinuous change in the behavior from 0.5 kbar to 2.9 kbar. The change in normal state value of the resistivity likely reflects the change in structure which we anticipate with increasing pressure. The superconducting transition temperature decreases monotonically with pressure, although as shown in figure 6b there is a change in slope of \( T_c \) versus pressure upon entering the high pressure phase. (At 25 kbar (not shown) there was no superconductivity observed down to 1.8 K.) At pressures above 4 kbar we suggest the system is structurally homogeneous, and thus our results show that the collapsed tetragonal phase of transition-metal pnictides in the ThCr\(_2\)Si\(_2\) structure can support superconductivity.

**Discussion:**

Several results from the ambient pressure data of SrNi\(_2\)P\(_2\) are suggestive of a fully gapped BCS superconductor, including the fit to the heat capacity data, the small value of \( H_{c2} \) and \( \kappa \). Band structure calculations for SrNi\(_2\)P\(_2\) give a density of states \( N(E_F) = 43 \) States/Ry cell\(^2\). This gives an electron-boson renormalization \( \lambda = 1.02 \), from the expression \( \gamma = \pi^2 k_B^2 N(E_F)/(1 + \lambda)/3 \), using the experimentally measured \( \gamma = 15 \) mJ/molK\(^2\). This is certainly sufficient to explain superconductivity in an electron-phonon pairing scenario. For example, using the simplified McMillan formula\(^2\)

\[
T_c = \frac{\Theta_D}{1.45} \exp \left[ -\frac{1.04(1 + \lambda)}{\gamma - \mu^*(1 + 0.62\lambda)} \right]
\]

and a very conservative estimate of \( \mu^* = 0.3 \) gives \( T_c = 4.5 \) K. Furthermore, calculations show that BaNi\(_2\)P\(_2\) has a larger density of states \( (\gamma)^{th} = 9.32 \) mJ/molK\(^2\) which is consistent with its larger superconducting transition temperature \( (T_c = 2.7 \) K\(^2\)). In addition, low temperature thermal conductivity data provide compelling evidence for fully gapped superconductivity in the related material BaNi\(_2\)As\(_2\). While not definitive, the accumulation of evidence suggests that SrNi\(_2\)P\(_2\) is a conventional BCS superconductor.

An open question is whether the pairing mechanisms of the Fe based systems and the Ni based compounds are related. On the basis of band structure calculations it has been argued that both \( T = Fe \) and \( T =
Ni lie close to a magnetic instability; however it remains the case that none of the Ni based systems possess superconducting transition temperatures in excess of 5 K, nor do they have evidence for magnetism. Density functional calculations suggest that the two systems have unrelated pairing mechanisms, based on the fact that they are unable to reproduce the high transition temperatures of the Fe-based compounds. However, it remains a possibility that the pairing mechanisms of the Ni-based systems are merely not as optimized for superconductivity as their iron-based cousins.

It is rather remarkable that superconductivity has been found in many of the nickel analogs for which the iron-based pnictide compounds also superconduct. Figure 7 shows that even the trend of the maximum superconducting transition temperature decreases monotonically from ReX(O,F) to BaX$_2$ to SrX$_2$ to CaX$_2$ irrespective of whether X = FeAs, NiAs, or NiP. A possible interpretation of this trend is that $T_c$ is suppressed with increasing dimensionality, or in other words, as the electronic structure becomes more isotropic. Comparison between the ZrCuSiAs and ThCr$_2$Si$_2$ structure types has already established that the electronic structure of the systems in the ThCr$_2$Si$_2$ structure are more 3-dimensional than those in the ZrCuSiAs structure. Within the ThCr$_2$Si$_2$ structure this can be further understood from the decreasing ionic radius in going from Ba to Sr to Ca. Consequently, the pnictide atoms are closer together allowing for stronger hybridization along the c-axis. Eventually the decreasing pnictide-pnictide distance will lead to the collapsed tetragonal state where the interlayer pnictides adopt a bonding configuration, which should be the most 3-dimensional due to the increased P-P hybridization along the c-direction, and hence the least favorable for superconductivity. Our results, which show that superconductivity in SrNi$_2$P$_2$ is suppressed upon entering the collapsed tetragonal phase, further support the notion that increased 3-dimensionality found in the collapsed tetragonal state at higher pressures is detrimental for superconductivity. Further work is needed to determine how precisely dimensionality in terms of structural, magnetic, and electronic anisotropy influences the correlation between families observed in figure 7. Irrespective of the origin of the trend, this work suggests that CaNi$_2$P$_2$ and CaNi$_2$As$_2$ will be superconducting at temperatures below 1.4 and 0.62 K, respectively.

**Conclusion:**
In conclusion, by $^{31}$P NMR we have demonstrated the lack of magnetism in SrNi$_2$P$_2$. We have also shown that SrNi$_2$P$_2$ is a bulk superconductor at ambient pressure at...
1.4 K. Upon entering the collapsed tetragonal phase with applied pressure, the superconducting transition temperature is monotonically suppressed. Further work is necessary to determine whether SrNi$_2$P$_2$ under pressure is the first transition metal-pnictide in the ThCr$_2$As$_2$ structure to possess bulk superconductivity, or whether a similar unknown mechanism as occurs in CaFe$_2$As$_2$ is at play. The suppression of $T_c$ with pressure and across families of compounds demonstrates the notion that increased 2-dimensionality is a mechanism through which higher $T_c$s can be achieved.

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