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F. Ronning, E.D. Bauer, T. Park, N. Kurita, T.W. Klimczuk, R. Movshovich, A.S. Sefat, D. Mandrus, J.D. Thompson
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= anyeved Nickel"

⁽Ni₂X₂ (X=pnictide, chalcogenide, or B) Based Superconductors

F. Ronning¹, E.D. Bauer¹, T. Park^{1,2}, N. Kurita¹, T. Klimczuk^{1,3}, R. Movshovich¹, A.S. Sefat⁴, D.

Mandrus⁴, J.D. Thompson¹

¹ Los Alamos National Lab. Los Alamos, NM 87545 USA

² Department of Physics, Sungkyunkwan University, Suwon 440-746, Korea

³ Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-952 Gdansk, Poland

⁴ Material Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Abstract

We review the properties of Ni-based superconductors which contain Ni_2X_2 (X=As, P, Bi, Si, Ge, B) planes, a common structural element to the recently discovered FeAs superconductors. We also compare the properties of the Ni- and Fe-based systems from a perspective of electronic structure as well as structure-property relations.

Pacs: 74.62.-c, 74.70.-b, 74.25.-q

Keywords: superconductors, nickel-based

Introduction:

Even before superconductivity was found in LaFeAs(O,F) at 26 K¹ it was known that a Ni analog LaNiPO superconducts at 4.3 K^{2,3}. While many compounds containing Fe₂As₂ planes with transition temperatures well above 5 K have been found (e.g. 4,5,6,7), to date, none of the nickel analogs (unless one includes the nickel borocarbides) have T_cs exceeding 5K^{8,9,10,11,12,13,14,15,16,17,18}. There are two possible reasons for this: (1) superconductivity in the nickel compounds has no relation to the iron based systems and is likely a conventional phonon mediated BCS s-wave superconductor, or (2) the pairing mechanism is in fact the same as the iron based system, but the conditions for superconductivity are not nearly as optimized for the Ni-based systems as they are for the Fe-based systems. At this time, one can not definitively conclude which scenario is correct.

In this review, we first examine the properties of Ni-based superconductors which contain the Ni_2X_2 (X = As, P, Bi, Si, Ge, B) PbO-type structure. We attempt to identify common features and then look at details learned from various compound specific studies and/or properties. In the second half of the review we attempt to compare the Ni systems to the Fe analogs. Specifically we compare band structure calculations and structural relationships. When examined independently, the majority of evidence suggests that the Ni-based systems are simple conventional BCS superconductors. However, the similarity of several relationships among the Fe- and Ni-based compounds suggests some deeper connections between the two compounds. We conclude with some open questions specific to Ni-based compounds.

Properties of Ni based compounds:

Having a low superconducting transition temperature is not sufficient reason to dismiss a compound as uninteresting. For example, many heavy fermion superconductors¹⁹ as well as $Sr_2RuO_4^{20}$ are well established unconventional superconductors with T_c 's less than 3 K. At the same time, one should not presume that structural similarity guarantees similar physics. Certainly, $(La,Ba)_2CuO_4^{21}$, $Sr_2RuO_4^{20}$, and $(Ba,K)BiO_3^{22}$ all have the perovskite structure, but each are believed to have entirely different mechanisms for superconductivity. Consequently, we begin by reviewing the properties of the Ni-based superconductors which contain the puckered Ni_2X_2 planes, common in the higher temperature Fe-based systems, without consideration of their Fe counterparts. For the moment we exclude the nickel-borocarbides^{23,24} and -boronitrides²⁵ from our discussion, despite them having this essential structural element as shown in figure 1. Implicit in our discussion will be the blind assumption that all these Ni-based systems have the same superconducting pairing mechanism.

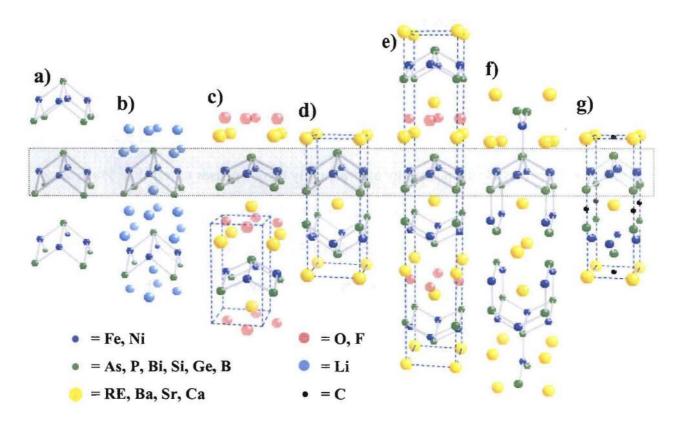


Figure 1. (color online) The crystal structure-types [a) PbO, b) Cu₂Sb, c) ZrCuSiAs, d) ThCr₂Si₂, e) Pr₃Cu₄P₄O₂, f) U₃Ni₄Si₄, g) YNi₂B₂C] which support superconductivity for either T = Fe (e.g. α -FeSe, LiFeAs, LaFeAs(O,F), (Ba,K)Fe₂As₂ for (a), (b), (c), and (d) respectively) and/or T = Ni (See table 1 for compounds with structures of (c), (d), (e), and (f)). All have in common the T₂X₂ structural element highlighted in the figure. RE = Rare Earth. (g) illustrates the same structural element in the borocarbide structure.

Figure 1, displays the crystal structures which contain the checkerboard Ni₂X₂ planes and have been found to be superconducting with Ni. The structure types include ZrCuSiAs, ThCr₂Si₂, Pr₃Cu₄P₄O₂, and U₃Ni₄Si₄. Table 1 lists the known superconducting Ni-based compounds along with their properties. As stated previously, the most significant observation is that none of the compounds contain superconducting transition temperatures above 5 K. The superconducting upper critical field H_{c2} is rather small in general, with the exception of ~5 T in doped LaNiAsO and 1.2 T in La₃Ni₄Si₄. The density of states at the Fermi level is small in all compounds, with Sommerfeld coefficients y ranging from 4.35 mJ/(mol-Ni K²) in SrNi₂As₂ to 9.23 mJ/(mol-Ni K^2) in La₃Ni₄Si₄. The cases where H_{c2} is small and specific heat or magnetization have been measured, reveal that the systems can have very small Ginzburg-Landau parameters κ (near the border between type I and type II) most notably $\kappa = 2.1$ in SrNi₂P₂. The specific heat jump at T_c is often less than the weak coupling BCS value of $\Delta C / \gamma T_c = 1.43$. This is rather peculiar, as Xray measurements exclude the possibility of structurally unique phases to less than 5% in these cases, which would suggest a more exotic interpretation. However, it is still possible that the reduced jump is due to impurities, either through pair breaking effects²⁶, or by an impurity "phase" which is structurally similar, but differs more subtlely, for example, through site substitution²⁷ or nickel vacancies²⁸.

Table 1: Properties of Ni-based superconductors which possess a common Ni_2X_2 structural unit. Samples are powders unless otherwise noted.

a <u>-</u>	from	McN	Aillan	formula	1
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	T _c (K)	$H_{c2}(0)(T)$	H _{c1} (Oe)	γexp (mJ/mol -Ni K ²)	γ _{th} (mJ/mol -Ni K ²)	λ	$\left \begin{array}{c} \Theta_{\mathrm{D}} \\ (\mathrm{K})^{\mathrm{c}} \end{array} \right $	$\Delta C/\gamma T$	refs
LaNiPO ^s	4.3 ^{b,e}	~0.2 ^{d,e}	25@1.8K ^e		3.32				2,3,29
La ₃ Ni ₄ P ₄ O ₂	2.2 ^c	0.59 ^d	520 ^e	6.22		0.5 ^a	357	1.25	8
BaNi ₂ P ₂ ^s	2.7 ^d	0.16 ^{fh} , 0.065 ^{gh}	50@2K ^{ef} , 80@2K ^{eh}		4.66				9,30,31
SrNi ₂ P ₂ ^s	1.4 ^c	0.039 ^{c,f,g}	88 ^c	7.5	3.72 ¹	1.02 ^j	348	1.27	10,30
LaNiAsO	2.75 ^b	~0.2 ^e	15@1.8K ^e		3.81				11,32
LaNiAs(O,F)	3.8 ^{b,c}	4.6 ^b		7.3		0.92 ^{j,k}		1.9	12
(La,Sr)NiAsO	3.7 ^b	5.5 ^b							13
BaNi ₂ As ₂ ^s	0.68 °	0.11 ^{c,f}	5°	6.15	4.19 ⁱ	0.47 ^j	206	1.31	14,33,34
SrNi ₂ As ₂ ^s	0.62°	0.015 ^{f,h} , 0.021 ^{g,h}		4.35			244		15
LaNiBiO _{1-x}	4.25 ^b	~3 ^b			5.39				16,35
GdNiBiO	4.5 ^b	2.5 ^b							17
La ₃ Ni ₄ Si ₄	1.0 ^c	1.2 ^b	107 ^e	9.23		0.4 ^a	321	1.32	18,36
La ₃ Ni ₄ Ge ₄	0.7 °	0.26 ^b	68 ^e	8.63		0.4 ^a	256	0.95	18,36

 b = determined by resistive onset

 c = Determined by C_{p}

^d = determined by $\rho=0$

e = from magnetization measurements

- f = H//ab
- $^{g} = H//c$

 $^{h} =$ from resistive midpoint

i = does not fully account for the structural transformation from the ThCr₂Si₂ structure

 $^{j} = (\lambda = \gamma_{exp} / \gamma_{th} - 1)$

^k = use γ_{th} from LaNiAsO

s = single crystal

A major question is whether any competing phases such as magnetism can be found in the Ni-

based systems. A few systems show structural transitions, such as $BaNi_2As_2$ and $SrNi_2P_2$. By

analogy with AFe₂As₂ (A=Ba, Sr, Eu, Ca)^{38,39,40,41,42}, one can speculate whether a structural and

magnetic transition are coincident. However, to date there is no evidence for magnetism in any

of the Ni-based systems, with the exception of ${\rm La_3Ni_4P_4O_2}$ which displays an enhanced Wilson

ratio⁸. Preliminary neutrons measurements⁴³ have failed to find magnetism in BaNi₂As₂ at low

temperatures, possibly due to the strong twinning associated with the structural transition itself. Similarly, ³¹P NMR failed to observe magnetism in $SrNi_2P_2^{10}$. Consequently, it appears that magnetism is very weak (if at all present) in the Ni-based systems.

System specific studies/properties:

$La_3Ni_4P_4O_2$

La₃Ni₄P₄O₂ is a particularly interesting compound in the family of Ni-based superconductors. The structure is that of alternating layers of LaNiPO and LaNi₂P₂. The former is a superconductor with $T_c = 4.3$ K, while the latter does not superconduct down to 1.8 K. One would anticipate that the dimensionality of La₃Ni₄P₄O₂ lies between LaNiPO (more 2-D) and LaNi₂P₂ (more 3-D), and with a $T_c = 2.2$ K La₃Ni₄P₄O₂ could be used to support the argument that reduced dimensionality is a means for achieving higher transition temperatures. However, band structure calculations contradict the naïve assumption that La₃Ni₄P₄O₂ is more 3-D than LaNiPO⁴⁴. Another interesting aspect of this crystal structure, is that the Ni₂P₂ planes have an asymmetric charge reservoir layer to either side, which may also influence T_c⁸.

$BaNi_2As_2$

Single crystals of BaNi₂As₂ have been grown by both Pb flux¹⁴ and self flux⁴⁵. The superconducting transition temperature as well as the structural transition temperature are independent of the growth technique, indicating that site substitution by the Pb flux, as occurs in BaFe₂As₂²⁷, does not occur here. BaNi₂As₂ has a structural transition at 130 K which possesses very strong twinning. It has been identified as a tetragonal to triclinic structural transition⁴⁵, and contrary to other structural transitions in the ThCr₂Si₂ structure, it is relatively insensitive to pressure and there is no enhancement of superconductivity up to 2.5 GPa⁴⁶. Due to the similarity

of the structural transition to the ones found in AFe_2As_2 (A = Ba, Sr, Ca, Eu) it was suggested that magnetism may also be involved in the transition. However, as mentioned above, to date there has been no evidence for magnetism in any of the Ni-based systems.

Bulk superconductivity is well established by heat capacity, AC magnetic susceptibility, thermal conductivity, and resistivity. From the thermal conductivity data and band structure calculations a mean free path $\ell = 70$ Å is estimated, and places BaNi₂As₂ in the dirty limit ($\ell/\xi < 1$) when compared with the coherence length $\xi = 550$ Å estimated by H_{c2}. The heat capacity data in figure 2a can be integrated, and the change in free energy equated to the thermodynamic critical field. This gives a thermodynamic critical field H_c = 73.1 Oe. Thus, from the relationships $\kappa = H_{c2}/\sqrt{2}H_c = H_c/\sqrt{2}H_{c1} = \lambda/\xi$, one finds BaNi₂As₂ is a type II superconductor with $\kappa = 11$, H_{c1} = 5 Oe and $\lambda = 6000$ Å.

As shown in figure 2, the heat capacity data is well fit by a BCS s-wave expression, and more importantly the thermal conductivity shows concave field dependence to the residual linear term κ_0/T . This is strong evidence that BaNi₂As₂ is a fully gapped superconductor, as nodal planes would create an easily distinguishable convex field dependence to the thermal conductivity (e.g. $\kappa_0/T \propto \sqrt{H}$ for line nodes)³³. Furthermore, as can be seen in figure 4, the Fermi surface is sufficiently complex to rule out the possibility that the nodal planes (for example of an s± state) simply happen not to intersect the Fermi surface.

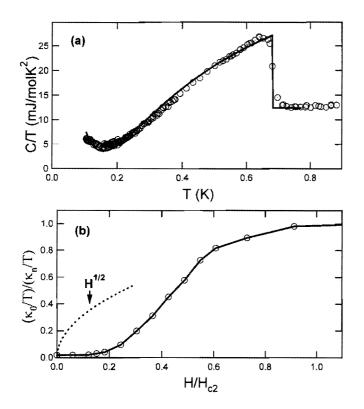


Figure 2. (a) Heat capacity data of $BaNi_2As_2$ which is well fit (solid line) by a s-wave BCS expression plus a low temperature nuclear Schottky term (discussed in ref³³). (b) Field dependence of the residual linear term κ_0/T normalized by the normal state value above H_{c2} . The concave dependence is anticipated for fully gapped superconductors, while convex behavior is expected for superconductors with nodes in the superconducting order parameter. Specifically, \sqrt{H} is expected for line nodes as shown by the dashed line.

EuNi₂As₂

While both BaNi₂As₂ and SrNi₂As₂ are superconducting near 0.65 K, from resistivity data (not shown)⁴⁷ EuNi₂As₂ is not superconducting down to 0.03 K despite Eu²⁺ having a similar ionic size to Sr^{2+} . In doped EuFe₂As₂, the Eu moments have an interesting interplay between magnetic order, and superconductivity in Fe-planes, with maximum transition temperatures similar to that found in doped $SrFe_2As_2^{48}$. In the nickel compound the onset of magnetic order of the Eu moments at 14 K^{49,50} appears to be too much for superconductivity in the Ni₂As₂ sublattice to overcome.

$SrNi_2P_2$

SrNi₂P₂ is unique among the Ni-based systems in the ThCr₂Si₂ structure, as it also possesses a structural transition into the so called collapsed tetragonal phase at relatively low pressures^{51,52}. At room temperature this occurs at 4kbar. CaFe₂As₂ possesses a similar structural transition under pressure⁵³, and depending on the pressure transmitting medium used, one does^{54,55} or does not⁵⁶ find evidence for superconductivity. At ambient pressure SrNi₂P₂ undergoes a structural phase transition at 325 K from a high temperature tetragonal to low temperature orthorhombic structure, which may be thought of as a precursor to the collapsed tetragonal phase. At low temperature some of the P atoms in neighboring planes possess a bonding configuration, whereas they were completely non-bonding at high temperatures. T_c is 1.4 K at ambient pressure. With applied pressure all the P atoms adopt a bonding configuration as the system enters the "collapsed tetragonal" phase which has the same symmetry (but smaller volume and presumably more 3D) as the high temperature tetragonal phase at ambient pressure. It is found that superconductivity is still observed in this state, although the transition temperature is substantially reduced compared with the ambient pressure result¹⁰. This again supports the notion that reduced dimensionality is better for superconductivity.

Doping Studies

Relatively little has been done with regards to chemical substitution in Ni based systems. However, the effects of doping on LaNiAsO are remarkable. Both hole doping with Sr replacing La^{13} , and electron doping with F replacing O^{12} *increases* the superconducting transition temperature as shown in figure 3. H_{c2} is also increased by a factor of nearly 20 in the doped system compared to the parent compound. Interestingly, the pressure dependence of T_c is nonmonotonic for both LaNiPO and LaNiAsO⁵⁷, an unusual behavior for conventional superconductors and resembling that of LaFeAs(O,F)⁵⁸. Sr doping into GdNiBiO also has a slight increase in T_c^{17} . For completeness, we mention that several substitution studies have also been done on SrNi₂P₂, but only the influence on the structural transition was investigated⁵⁹.

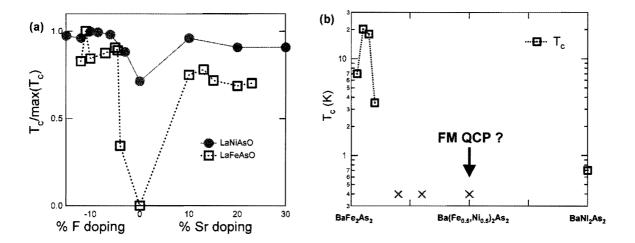


Figure 3. (a) Doping phase diagram of (La,Sr)TAs(O,F) (T = Ni or Fe). Values reproduced from refs ^{1,12,13,60}. (b) Doping phase diagram of Ba(Fe,Ni)₂As₂. ×'s indicate lowest temperature measured without observation of superconductivity. Values reproduced from refs ^{14,45,61}

Electronic Structure

Band structure calculations of Ni compounds predict a density of states at the Fermi level which suggests roughly a factor of 2 mass renormalization, when compared with the Sommerfeld coefficient as measured by specific heat (see table 1). dHvA measurements on BaNi₂P₂ also provide evidence that the mass renormalization $m_{exp}/m_{band} \approx 2^{62}$. In addition, calculations of the phonon spectra and the $\alpha^2 F$ function provide sufficient glue ($\lambda = 0.58$ and 0.76 for LaNiPO and BaNi₂As₂, respectively) to produce transition temperatures up to 4 K, sufficiently above the observed transition temperatures^{29,34}. Whether the experimentally measured mass renormalization is predominantly due to phonons or contains additional correlation effects is currently unknown.

It should be noted that the theoretically stable position of the pnictide atom relative to the Ni plane (the z parameter) agrees with the experimentally measured position. This supports the experimental results that magnetism and/or spin fluctuations do not appear relevant for the Ni-based compounds.

Independent Conclusion of Ni-based systems

In conclusion, there is very little evidence that suggests that the Ni based systems by themselves are anything other than conventional BCS superconductors. The evidence that the system is fully gapped comes from field dependent thermal conductivity measurements³³, while the most anomalous feature is the increase in transition temperature of LaNiAsO with doping^{12,13}.

Relationship to Fe-based systems:

Electronic structure

We begin our comparison of the Fe and Ni-based systems from the band structure perspective. One main difference between Fe and Ni is clearly the 2 additional electrons which Ni possesses relative to Fe. Indeed, the band structures of Ni-based compounds^{16,31,34,35,44,29,32,62,63,64} are reasonably approximated by a rigid band shift relative to the Fe analogs. A consequence of this is that the Fermi surfaces of these compounds can differ rather markedly, and the carrier density is much larger in the Ni-analogs⁶⁵. The small pockets which existed in the Fe compound now are larger sheets crossing through much of the Brillouin zone (see figure 4).

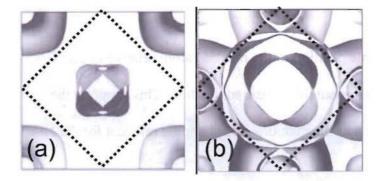


Figure 4: Fermi surface differences from Fe compounds to Ni compounds, here for (a) $BaFe_2As_2$ from ref. ⁶⁶ and (b) $BaNi_2As_2$ from ref. ³⁴ projected onto the ab-plane. Dashed line indicates the surface where the superconducting order parameter is expected to change sign in the s± pairing state. Note that in (a) it does not intersect the Fermi surface, and thus the system will be fully gapped even in the s± state, while in (b) gapless (nodal) excitations are expected.

A doping study of Ba(Fe,Ni)₂As₂ appears to generally support the band structure. The phase diagram in figure 3b can be used to illustrate this as well as highlight the two biggest differences already alluded to between the Fe-based systems, and the Ni-based systems. Namely, in the Fe based systems the parent compounds possess antiferromagnetism, which is suppressed with doping or pressure giving way to a dome of superconductivity. In the Ni compounds the parent compounds themselves superconduct, and there is no evidence to date for any proximity to magnetism (aside from the enhanced Wilson ratio in La₃Ni₄P₄O₂⁸), despite early calculations which suggested that they also lie close to a magnetic instability³². The other big difference is the roughly factor of 20 difference between the T_c of the doped Fe system to that of the Ni analog. In fact, this is the basis on which band structure calculations claim that the Fe-systems must be unconventional, while the Ni ones may not be. Not surprisingly, one can account for the magnitude of T_c in the Ni based systems via phonon-mediated pairing with a few reasonable assumptions^{29,34}, however this is not the case for the Fe-based systems^{67,68}.

Returning to the band structure, there is a Van-Hove singularity in the density of states at an intermediate doping level, which by a simple Stoner criteria suggests a ferromagnetic instability. Co lies between Fe and Ni on the periodic table, and indeed, LaCoAsO and LaCoPO are ferromagnets ($T_C = 66$ K and 43 K respectively)^{69,70}, and BaFeNiAs₂ and BaCo₂As₂ are suggested to lie in close proximity to a FM quantum critical point^{45,71}. The Sommerfeld coefficient of the latter two compounds is more than a factor of 2 larger than either BaFe_{1.4}Ni_{0.6}As₂ or BaNi₂As₂, consistent with the enhanced density of states from the Van-Hove singularity.

Surprisingly the renormalization effects on the electronic structure between the two end members appear to be similar. dHvA results on AFe₂As₂⁷², LaFePO⁷³, and BaNi₂P₂⁶² all suggest a mass renormalization $m_{exp}/m_{band} \sim 2$. In the case of the Fe compounds this result is supported by ARPES measurements⁷⁴. Heat capacity measurements also generally support a mass renormalization of 2 in most cases for both systems. Thus, while magnetism does not appear in the Ni-based systems, electronic correlations may still be just as significant. It would be interesting to see if calculations including correlation effects such as DMFT would support this view as it has for the Fe-based systems⁷⁵.

Structure-Property relationships.

Another empirical method for trying to find superconductors with higher T_c , is to attempt to identify structure-property relations that relate to T_c . With this in mind we list several structural parameters of the Ni-based superconductors in Table 2. So far clear structure- T_c relationships have been difficult to identify in the FeAs systems. Perhaps the best correlation to date has been

in the ZrCuSiAs structure type, where T_c appears to be a smoothly varying function of the As-Fe-As bond angle, with the optimum T_c obtained close to the ideal tetrahedral angle of 109.5 ° ⁷⁶. It is noted, that all of the Ni-based systems have an angle above 117° and are thus consistent with smaller T_c s, The exception to this is the borocarbide (discussed below) which is strikingly much closer to the ideal tetrahedral angle.

c' (and V') is the distance (and corresponding volume) between neighboring Ni_2X_2 planes.								
	a (Å)	c' (Å)	$V'(Å^3)$	c'/a	d_{Ni-Ni} (Å)	d_{Ni-X} (Å)	\angle_{XNiX}	refs
LuNi ₂ B ₂ C	3.464	5.316	63.78	1.53	2.449	2.102	110.94	77
LaNiPO	4.0453	8.1054	132.6	2.004	2.86	2.265	126.5	3
GdNiBiO								
LaNiBiO _{1-x}	4.073	9.301	154.3	2.284	2.880			16
LaNiAsO	4.1231	8.1885	139.2	1.986	2.915	2.3463	122.95	11
BaNi ₂ P ₂	3.947	5.91	92.071	1.497	2.791	2.259	121.7	51
$La_3Ni_4P_4O_2$	4.0107	8.232,	132.4,	2.052,	2.836	2.271,	120.8,	8
		4.858	78.2	1.211		2.306	124.0	
$SrNi_2P_2$	3.951 ^b	5.216 ^b	81.42 ^b	1.320 ^b	2.800 ^b	2.247-	117.82-	51
						2.299	123.68	
La ₃ Ni ₄ Si ₄	4.131,	11.79	203.4	2.839	2.938	2.427,	118.68,	78
	4.176 ^a					2.372	121.06	
La ₃ Ni ₄ Ge ₄	4.202,	12.02	213.0	2.85	2.989	2.447,	119.55,	78
	4.217 ^a					2.421	121.46	
BaNi ₂ As ₂	4.142	5.825	99.9	1.406	2.929	2.405	118.86	79
$SrNi_2As_2$	4.154	5.145	88.78	1.239	2.937	2.377	121.82	80

Table 2. Structural parameters of Ni based SC's in order of descending transition temperatures. c' (and V') is the distance (and corresponding volume) between neighboring Ni_2X_2 planes.

 a^{a} = a and b lattice parameters for the orthorhombic structure

^b = averaged parameters for low T structure

It is remarkable that despite the huge difference in T_c , several trends of T_c across different compounds appear to be similar in Ni and Fe based systems. For example, we have mentioned that T_c in the LaNiAsO system increases with both hole and electron doping, and roughly to the same value. While the parent LaFeAsO is not superconducting, both hole and electron doping produces very similar behavior to the Ni-compound as illustrated in figure 3a. It is also noted that in going from LaTXO to BaT₂X₂ to SrT₂X₂ to CaT₂X₂ a monotonic suppression in T_c is observed whether (T,X) = hole doped (Fe,As), (T,X) = (Ni,As), or (T,X) = (Ni,P), which can be seen in table 3. One possible origin for this trend is that dimensionality is reduced across this series. Certainly, arguments for reduced dimensionality enhancing T_c in the Fe-based materials have already been made⁸¹, and in this review we have suggested similar rationales to understand several observations in the Ni compounds (specifically La₃Ni₄P₄O₂ and SrNi₂P₂¹⁰).

Table 3: Comparison of superconducting transition temperatures across families in the ZrCuSiAs and ThCr₂Si₂ structure. Note the monotonically decreasing dependence of T_c in going either across a row or down a column. Values from refs ^{5,40,58,82} and table 1.

	T=Fe, X=As	T=Ni,X=P	T=Ni,X=As
LaTXO	43 K	4.3 K	2.75 K
BaT ₂ X ₂	38 K	2.7 K	0.68 K
SrT ₂ X ₂	37 K	1.4 K	0.62 K
CaT_2X_2	20 K		

Another perspective on table 3 would argue that T_c is monotonically suppressed in going from Fe_2As_2 to Ni_2P_2 to Ni_2As_2 planes irrespective of the host structure. Could this simply be a property of the intrinsic ability of electron pairs to condense in the various T_2X_2 layers?

Implications for similar and different pairing mechanisms.

If the Ni compounds do indeed have the same pairing mechanism as the Fe compounds, but simply are not as well optimized for superconductivity, the fully gapped nature of the $BaNi_2As_2$ implies that the s± state would be exceedingly difficult to realize. The reason is that due to the more complex Fermi surface in the $BaNi_2As_2$ system, it is much more difficult to find a nodal plane which does not intersect the Fermi surface in $BaNi_2As_2$. Hence, the s± state is not supported by the results on the nickel compounds to date. On the other hand, even if the pairing mechanisms are different, one can ask about the many empirical similarities that still exist between the Fe-based systems and the Ni-based systems. Perhaps, this is simply a statement of the notion that some crystal structures just happen to be good for superconductivity. For example the Perovskite structure supports d-wave $((La,Ba)_2CuO_4)^{21}$, p-wave $(Sr_2RuO_4)^{20}$, and s-wave $((Ba,K)BiO_3)^{22}$ pairing symmetries, while the ThCr₂Si₂ structure, to which all the transition-metal pnictide superconductors share a common T_2X_2 structural element, is already known to support spin-mediated (ie CePd₂Si₂)⁸³, valence-fluctuation-mediated (CeCu₂(Si,Ge)₂)⁸⁴, and phonon-mediated (ie. LaPd₂Ge₂⁸⁵) superconductivity. Does this imply that the ability to screen the Coulomb repulsion is an inherent property of a crystal structure regardless of the nature of the pairing potential?

Relationship to the borocarbides?

Throughout this review we have ignored the nickel borocarbides and boronitrides, despite the fact that they too contain Ni₂X₂ (X=B) planes as shown in figure 1g which would suggest that they may be related to the other Ni-based superconductors we have discussed above. The borocarbide systems have relatively high T_c (ie. 16.5 K for LuNi₂B₂C²³), and there is no magnetism associated with the Ni atoms (magnetism when present is due to the rare earths atoms in the structure, similar to REFeAsO or EuNi₂As₂). One potentially significant difference is that the ionic nature of the (T₂Pn₂)²⁻ (T = Fe, Ni; Pn = pnictide) is presumably altered for the Ni₂B₂ planes. The pairing symmetry is still unresolved with reports both for and against unconventional superconductivity⁸⁶. It would certainly be interesting if a Fe, Ru, or Os borocarbide superconductor could be found.

Conclusions and open questions:

Clearly, more work is needed to elucidate the relationship between Fe-based and Ni-based pnictides. The fact that so many Ni analogs of the Fe superconductors also superconduct and vice versa suggests several interesting materials to attempt to synthesize including $La_3Fe_4P_4O_2$, AFe_2P_2 (A = Ba, Sr, Ca), Fe-, Ru-, or Os- based borocarbides, LiNiAs, and $La_3Fe_4Ch_4$ (Ch = chalcogenide). It would also be preferable to have more direct comparisons of similar techniques on both the Fe and Ni-based systems. This suggests performing ARPES, NMR, penetration depth, and DMFT calculations on the Ni-systems.

In conclusion, we have shown that the stoichiometric compounds containing Ni_2X_2 (X = pnictide or chalcogenide) planes when examined outside the context of the FeAs superconductors appear to be conventional BCS phonon-mediated superconductors. However, why T_c increases with doping in LaNiAsO, why the mass renormalization is similar to the Fe-analogs in the absence of magnetism, and why structure-property relations appear so similar between the two remain to be understood.

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