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FAST TRACK COMMUNICATION

The first order phase transition and superconductivity in $BaNi_2As_2$ single crystals

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Abstract
We report the synthesis and physical properties of single crystals of stoichiometric $BaNi_2As_2$ that crystallizes in the $ThCr_2Si_2$ structure with lattice parameters $a = 4.112(4)$ Å and $c = 11.54(2)$ Å. The resistivity and heat capacity show a first order phase transition at $T_0 = 130$ K with a thermal hysteresis of 7 K. The Hall coefficient is weakly temperature dependent from room temperature to 2 K where it has a value of -4×10^{-10} Ω cm Oe^{-1}. The resistivity, ac susceptibility, and heat capacity provide evidence for bulk superconductivity at $T_c = 0.7$ K. The Sommerfeld coefficient at T_c is 11.6 ± 0.9 mJ mol^{-1} K^{-2}. The upper critical field is anisotropic with initial slopes of $dH_{c2}^{c}/dT = -0.19$ T K^{-1} and $dH_{c2}^{ab}/dT = -0.40$ T K^{-1}, as determined from the resistivity.

(Some figures in this article are in colour only in the electronic version)

The large superconducting transition temperatures found in the oxypnictide system has stimulated a great deal of research activity world-wide. Perhaps, even more remarkable than the large transition temperatures (up to 55 K for SmFeAs(O,F) [1]) is the large tunability these systems possess. Superconductivity has been found in RTPn(O,F) (ZrCuSiAs structure type) at ambient pressure with rare-earth R = La, Ce, Pr, Nd, Sm, or Gd; transition metal T = Fe or Ni, and Pnictide Pn = P or As [1–12]. Some compounds require chemical substitution, while for others the parent compounds also superconduct. Furthermore, superconductivity has also been discovered in the related $ThCr_2Si_2$ structure type, where it has been found by doping AFe_2As_2 on the A site (with A = Ba, Sr, Ca, Eu) [13–17], under pressure in AFe_2As_2 [18–20], and at ambient pressure in the stoichiometric compounds $BaNi_2P_2$ [21], $LaRu_2P_2$ [22], $CsFe_2As_2$, and KFe_2As_2 [15].

The common structural element between the ZrCuSiAs and $ThCr_2Si_2$ structure types are T_2Pn_2 layers which are alternately stacked with R_2O_2 or A layers in the RTPnO and AT_2Pn_2 families, respectively. The fact that the highest transition temperatures in both families occur in compounds containing Fe_2As_2 layers suggests that the T_2Pn_2 layers are the active layers while the R_2O_2 or A layers act as a spacer that can fine tune the electronic structure of the T_2Pn_2 layer and act as a charge reservoir layer, but do not control the physics. Since superconductivity has been found in LaNiAsO [9], one might expect that superconductivity would also be found in the $ThCr_2Si_2$ structure type with an active Ni_2As_2 layer.

Following this reasoning, we have synthesized single crystals of $BaNi_2As_2$. We find a first order phase transition at $T_0 = 130$ K (cooling) with 7 K thermal hysteresis. By analogy with AFe_2As_2 (A = Ba, Sr, Ca) [16, 23–26] we identify this transition as a magnetic spin-density wave (SDW) transition concomitant with a structural transition. Here we show that $BaNi_2As_2$ is also a bulk superconductor at $T_c = 0.7$ K, well below the first order phase transition T_0.

Single crystals of $BaNi_2As_2$ were grown in Pb flux in the ratio Ba:Ni:As:Pb = 1:2:2:20. The starting elements were

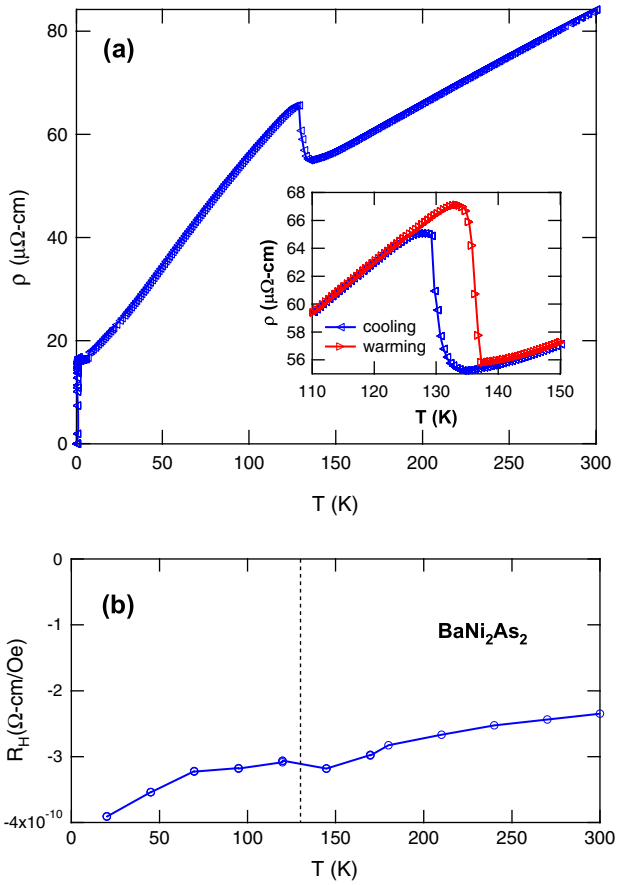

Figure 1. Transport properties of $BaNi_2As_2$. (a) In-plane resistivity ($I \parallel ab$). The inset demonstrates the thermal hysteresis at the transition. (b) Hall coefficient R_H of $BaNi_2As_2$. The dashed line indicates the first order transition temperature.

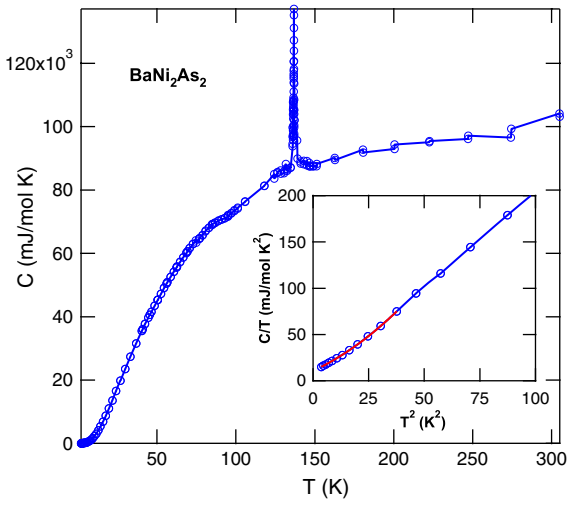

Figure 2. Specific heat versus temperature is shown for $BaNi_2As_2$. The inset displays the low temperature heat capacity. The solid line is a fit to $C/T = \gamma + \beta T^2 + \alpha T^4$.

placed in an alumina crucible and sealed under vacuum in a quartz ampoule. The ampoule was placed in a furnace and heated to 600 °C at 100 °C h^{-1}, and held at that temperature

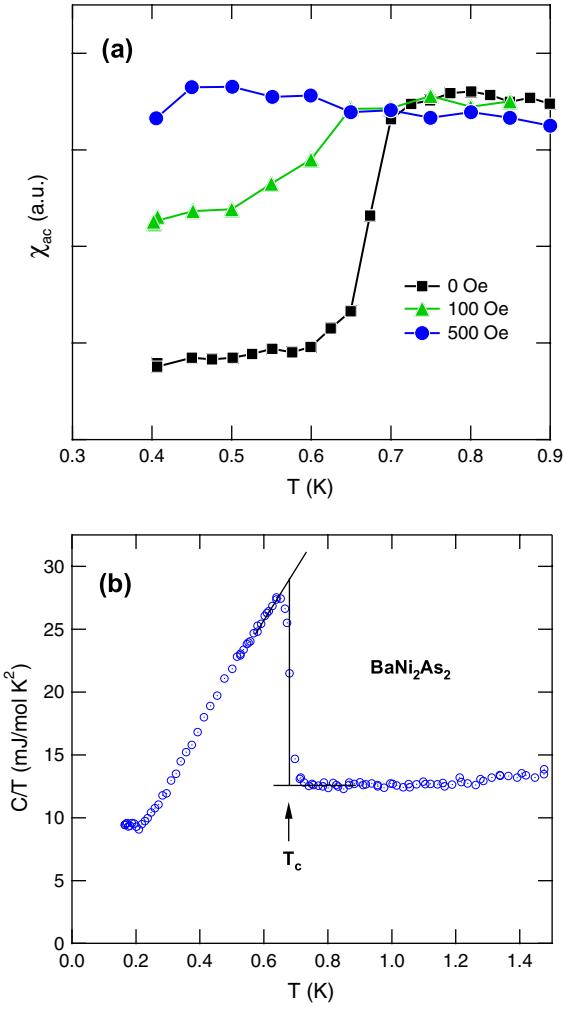

Figure 3. (a) ac magnetic susceptibility $\chi_{ac}(T)$ of $BaNi_2As_2$ with applied magnetic field. (b) Low temperature specific heat of $BaNi_2As_2$.

for 4 h. This sequence was repeated at 900 °C and at a maximum temperature of 1075 °C, with hold times of 4 h, each. The sample was then cooled slowly (~7 °C h^{-1}) to 650 °C, at which point the excess Pb flux was removed with the aid of a centrifuge. The resulting plate-like crystals of typical dimensions $1 \times 1 \times 0.1$ mm^3 are micaceous and air sensitive and are oriented with the c-axis normal to the plate. $BaNi_2As_2$ crystallizes in the $ThCr_2Si_2$ tetragonal structure (space group no. 139). Single crystal refinement [$R(I > 2\sigma) = 5.37\%$] at room temperature gives lattice parameters $a = 4.112(4)$ Å and $c = 11.54(2)$ Å and fully occupied atomic positions Ba 2a(0, 0, 0), Ni 4d(0.5, 0, 0.25) and As 4e(0, 0, z) with $z = 0.3476(3)$ consistent with previous reports [27, 28]. Powder x-ray diffraction data was consistent with the single crystal diffraction data.

Specific heat measurements were carried out using an adiabatic relaxation method in a commercial cryostat from 2 to 300 K, and in a dilution refrigerator down to 150 mK. Electrical transport measurements were performed using a LR-700 resistance bridge with an excitation current of 0.2 mA, on samples for which platinum leads were spot welded. X-ray data were collected at room temperature on a Bruker

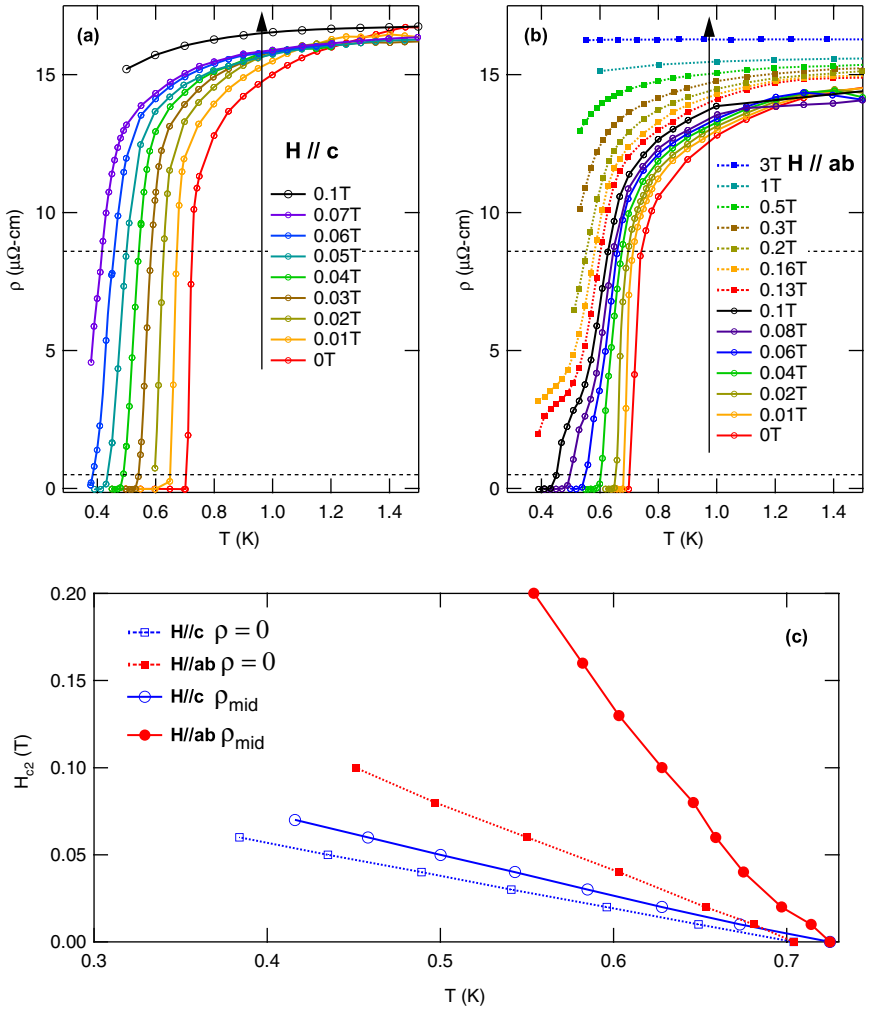

Figure 4. Evidence for superconductivity from the resistive transition for $H \parallel \hat{c}$ (a) and $H \parallel \hat{ab}$ (b). (c) Upper critical field for $H \parallel \hat{c}$ and $H \parallel \hat{ab}$ as determined by the dashed lines in panels (a) and (b). The current was always perpendicular to the magnetic field.

APEXII diffractometer, with charge-coupled-device detector, and graphite monochromated Mo Kα (λ = 0.710 73 Å) radiation. The data were corrected for absorption and Lorentz-polarization effects.

Resistivity and heat capacity shown in figures 1 and 2, respectively, provide clear evidence for a first order transition that occurs at 130 K upon cooling, and at 137 K upon warming, consistent with earlier magnetic susceptibility results on polycrystalline samples [28]. The resistivity anomaly is very similar to that observed in $CaFe_2As_2$ [16, 25, 26] with a RRR ($=\rho(300\text{ K})/\rho(4\text{ K})$) of 5, while the absolute magnitude of the resistivity is more than an order of magnitude less than in the AFe_2As_2 compounds. The thermal hysteresis of 7 K is clearly observed in the resistivity data shown as an inset to figure 1. The Hall coefficient is negative over the entire temperature range, and displays a weak anomaly at T_0. The value at 2 K is $R_H = -4 \times 10^{-10}$ Ω cm Oe^{-1}. The sharp anomaly at 137 K in the heat capacity data of figure 2 (taken upon warming) is also consistent with a first order phase transition. From 2 to 6 K the heat capacity data was fit to $C = \gamma T + \beta T^3 + \alpha T^5$. This yields a Sommerfeld coefficient $\gamma = 10.8 \pm 0.1$ mJ mol^{-1} K^{-2}. Assuming that the T^3 term is due solely to acoustic phonons, the β coefficient $=1.10 \pm 0.01$ mJ mol^{-1} K^{-4} gives a Debye temperature $\Theta_D =$ 206 K.

At low temperatures, ac susceptibility, heat capacity, and resistivity provide evidence for bulk superconductivity. As shown in figure 3(a) the onset of diamagnetism starts at 0.7 K and is estimated to be >50% volume fraction, by comparing the signal to that of a piece of Pb with a comparable volume. The low temperature heat capacity data on a second sample shown in figure 3(b) reveals a sharp anomaly at 0.68 K with a jump $\Delta C = 11.15$ mJ mol^{-1} K^{-1}. Taking the value of the Sommerfeld coefficient at T_c ($\gamma = 12.5$ mJ mol^{-1} K^{-2}) gives[4] the ratio $\Delta C/\gamma T_c = 1.31$. The large ratio confirms the bulk nature of superconductivity, but further work is necessary to determine whether the heat capacity data can reveal any sign of unconventional superconducting behavior.

From the resistivity data at low temperatures shown in figure 4 we can extract additional information. The resistivity sample has trace amounts of Pb impurities which gives a partial

[4] We attribute the difference in γ obtained from the data at T_c and the extrapolation from higher temperature to the difficulty in subtracting the addenda at low temperatures.

transition at 7.2 K. At roughly 1.5 K there is an additional downturn in the resistivity data, which then goes to zero abruptly at 0.7 K. Since the bulk transition occurs sharply at 0.7 K in zero field, we attribute the downturn at 1.5 K to an unknown impurity phase which is also superconducting. Upon application of a magnetic field, we estimate the upper critical field for both the bulk superconductor and the impurity phase. We extract the upper critical field, $H_{c2}(T)$ for $BaNi_2As_2$ by taking the temperature at which $\rho = 0.5\ \mu\Omega$ cm (the lower dashed line in figures 4(a) and (b)). This gives initial slopes of $dH^{ab}_{c2}/dT = -0.396$ T K^{-1} and $dH^{c}_{c2}/dT = -0.186$ T K^{-1} with an anisotropy of 2.1. From these initial slopes we estimate the zero temperature upper critical field $H_{c2}(0) = -0.7T_c dH_{c2}/dT_c$ [29] to be 0.19 T and 0.09 T for $H \parallel ab$ and $H \parallel c$, respectively, yielding a Ginzburg–Landau coherence length $\xi^{ab} = 420$ Å and $\xi^{c} = 610$ Å, using the formula $\xi = (\Phi/2\pi H_{c2}(0))^{1/2}$, where $\Phi = 2.07 \times 10^{-7}$ Oe cm^2 is the flux quantum. Surprisingly, for the magnetic field in the *ab*-plane the resistive anomaly develops a shoulder. Consequently, the upper critical field of the impurity phase, for which we obtain a rough estimate by taking the midpoint of the resistive transition, has even greater anisotropy than the bulk $BaNi_2As_2$ superconductor.

Whether superconductivity can coexist with the low temperature orthorhombic structure and/or the spin-density wave (SDW) ground state is unclear. While coexistence of SDW and SC order is observed in the phase diagram of some doped compounds (e.g. [2]), whether or not this is microscopic coexistence remains to be determined. Of the stoichiometric compounds which superconduct in either the ZrCuSiAs [8, 9, 11] or $ThCr_2Si_2$ [15, 18, 19, 21, 22] structure, to our knowledge, none have yet been shown to coexist with a magnetic ground state. Microscopic confirmation of a low temperature orthorhombic possessing a spin-density wave is still needed in $BaNi_2As_2$. However, the similarity of the first order anomaly here to those found in the AFe_2As_2 systems [16, 23–26] where an orthorhombic SDW state has been determined [30, 31] is suggestive that a similar situation occurs in $BaNi_2As_2$. Thus, the clear observation of bulk superconductivity below the first order transition in $BaNi_2As_2$, may constitute the first example of coexistence of these three order parameters in a system with active T_2Pn_2 layers.

The observation of bulk superconductivity at 0.7 K in $BaNi_2As_2$ completes a form of continuity with regards to the presence of superconductivity in going from the ZrCuSiAs structure type to the $ThCr_2Si_2$ structure type, independent of whether the active layers are Fe_2As_2, Ni_2P_2, or Ni_2As_2. When the active layers are Fe_2As_2, the stoichiometric materials possess SDW order, and require doping or pressure to produce superconductivity. In the cases of Ni_2P_2 and Ni_2As_2 layers, the stoichiometric parent compounds possess superconductivity in both structure types. The biggest difference with these comparisons is that $BaNi_2As_2$ has a first order phase transition, while LaNiAsO does not.

In conclusion, we have synthesized single crystals of $BaNi_2As_2$, which possesses both a first order transition at 130 K, which is likely a combined structural and magnetic transition, and superconductivity at 0.7 K. It will be interesting to study the dependence of doping, pressure, and isoelectronic substitution on these transitions to help elucidate the origin of superconductivity as well as the influence of competing orders.

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