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Renormalized behavior and proximity of $BaCo_2As_2$ to a magnetic quantum critical point

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We report synthesis and single-crystal measurements of magnetic, transport, and thermal properties of single crystalline $BaCo_2As_2$ as well as first-principles calculations of the electronic structure and magnetic behavior. These results show that $BaCo_2As_2$ is a highly renormalized paramagnet in proximity to a quantum critical point, presumably of ferromagnetic character and that $BaFeNiAs_2$ behaves similarly. These results are discussed in relation to the properties of $Ba(Fe,Co)_2As_2$ and $Ba(Fe,Ni)_2As_2$, which are superconducting for low Co and Ni concentrations.

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The discovery of high-temperature superconductivity in oxypnictide phases, prototype LaFeAs(O,F) by Kamihara and *et al.*[1] has led to strong interest in establishing the physical properties of these materials and the mechanism of superconductivity. Since the discovery, superconductivity has been found in a rather wide variety of compounds with Fe^{2+} square planar sheets. These include the oxypnictides, doped $ThCr_2Si_2$ structure compounds of, e.g., $BaFe_2As_2$,[2] LiFeAs,[3] and FeSe.[4] Remarkably, superconductivity can be produced in $BaFe_2As_2$ by alloying Fe with the other ferromagnetic 3*d* elements, Co or Ni,[5,6] as is also found in the oxypnictides.[7] Interestingly, both the Ni-based oxypnictide and $BaNi_2As_2$ are superconductors,[8–10] although the critical temperatures are much lower than in the Fe-based compounds and the pairing mechanism may be different[11,12] Also, LaCoAsO and LaCoPO are itinerant ferromagnets.[7,13]

The single crystals of $BaCo_2As_2$ were grown out of CoAs flux. The typical crystal sizes were $\sim 5\times 3\times 0.2$ mm^3. High purity elements (>99.9%, from Alfa Aesar) were used in the preparation of the crystals. First, CoAs binary was prepared by placing mixtures of arsenic pieces, and cobalt powder in a silica tube. These were reacted slowly by heating to 300 °C (dwell 10 h), to 600 °C (dwell 10 h), then to 900 °C (dwell 10 h). Then, a ratio of Ba:CoAs=1:5 was heated in an alumina crucible for 15 h at 1180 °C under a partial atmosphere of argon. This reaction was cooled at the rate of 2 °C/h, followed by decanting of CoAs flux at 1090 °C. The crystals were well-formed plates with the [001] direction perpendicular to the plane. Electron probe microanalysis of a cleaved surface of the single crystal was performed on a JEOL JSM-840 scanning electron microscope using an accelerating voltage of 15 kV and a current of 20 nA with an EDAX brand energy-dispersive x-ray spectroscopy (EDS) device. EDS analyzes indicated Ba:Co:As ratio of 1:2:2. The structural identification was made via powder x-ray diffraction using a PANalytical X'pert Pro MPD with an X'celerator position sensitive detector (Cu $K\alpha$ radiation). The cell parameters were refined from full pattern LaBail fits using the program FullProf.[14] The lattice parameters of $BaCo_2As_2$ are $a=3.9537(1)$ Å, and $c=12.6524(6)$ Å, in the $ThCr_2Si_2$ structure ($I4/mmm$, $Z=2$) in close agreement with the report of Ref. 15.

dc magnetization was measured as a function of temperature and field using a Quantum Design magnetic property measurement system (PPMS). Figure 1 shows the susceptibility in 1 kOe applied field along *c*- and *ab*-crystallographic directions. The susceptibility is weakly anisotropic and decreases with increasing temperature. At 1.8 K, $\chi_c=5.4\times 10^{-3}$ cm^3 mol^{-1} and $\chi_{ab}=3.8\times 10^{-3}$ cm^3 mol^{-1}. As seen in the inset of Fig. 1 the field dependent magnetization is linear at 1.8 K.

Temperature dependent electrical resistivity measurements were performed on a Quantum Design PPMS, measured in both the *ab* plane (ρ_{ab}) and *c* direction (ρ_c). As shown in Fig. 2, both ρ_{ab} and ρ_c decrease with decreasing temperature, revealing metallic behavior. However, the resistivity is much more anisotropic than the magnetic susceptibility. At room temperature $\rho_{ab}=0.07$ mΩ cm and $\rho_c=2.7$ mΩ cm, resulting in $\rho_c/\rho_{ab}\sim 39$. In analyzing the low-temperature data, we found that both ρ_{ab} and ρ_c exhibit quadratic temperature dependencies in a wide temperature range. Shown in the inset of Fig. 2 is the plot of $\rho_{ab}(T^2)$ and $\rho_c(T^2)$ between 1.8 and 71 K. Note that ρ_{ab} and ρ_c vary approximately linearly with T^2 below ~60 K. By fitting the resistivity data between 1.8 and 60 K using $\rho_{ab,c}=\rho_{ab,c}(0\text{ K})+AT^2$, we obtain the residual resistivity $\rho_{ab}(0\text{ K})=5.75$ $\mu\Omega$ cm, $\rho_c(0\text{ K})=0.22$ mΩ cm, and constant $A_{ab}=2.22\times 10^{-3}$ $\mu\Omega$ cm/K^2, $A_c=9.65\times 10^{-2}$ $\mu\Omega$ cm/K^2. These give the residual-resistivity-ratio ($\rho_{300\text{ K}}/\rho_{0\text{ K}}$) ~12

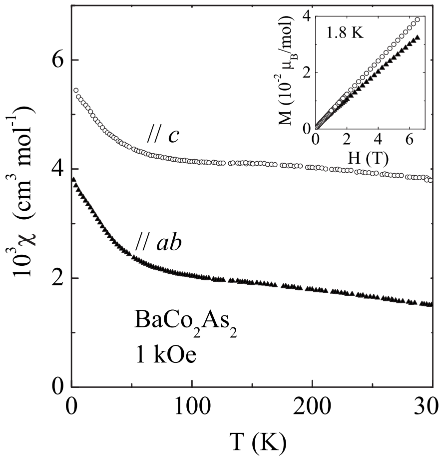

FIG. 1. Magnetic measurements for $BaCo_2As_2$ along the two crystallographic directions. The figure is the temperature dependence of the zero-field cooled magnetization in 1 kOe; inset is the field dependence of the magnetization at 1.8 K.

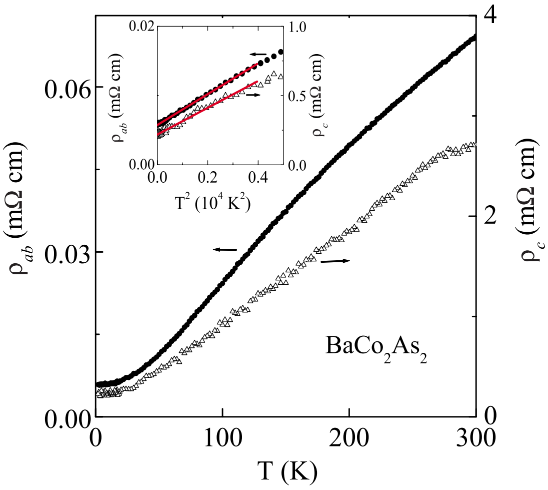

FIG. 2. (Color online) Temperature dependence of the resistivity of $BaCo_2As_2$ in zero field for the two crystallographic directions.

along both crystallographic directions, indicating good crystal quality. The quadratic temperature dependence of the electrical resistivity reflects the importance of the Umklapp process of the electron-electron scattering at low temperatures and is consistent with the formation of a Fermi-liquid state. Interestingly, the system shows little magnetoresistance under application is magnetic field up to 8 T.

Specific heat data, $C_p(T)$, were also obtained using the PPMS via the relaxation method. Figure 3 gives the temperature dependence of specific heat. Below ~7 K, C/T vs T^2 is linear (inset of Fig. 3) consistent with a Fermi liquid plus phonon contribution. In the temperature range of 1.9–~7 K, the fitted Sommerfeld coefficient, γ, is 8.2 mJ/(K^2 mol-atom) or 20.5 mJ/(K^2 mol-Co). This is a high value that would correspond to an electronic density of states (DOS) of 8.7 eV^{-1}/Co both spins. The mean-field Stoner criterion ($NI>1$, $I\sim 0.8$ eV per spin for $3d$ elements) for ferromagnetism would be strongly exceeded if this is interpreted as the bare electronic density of states for Co. The absence of magnetism therefore implies either strong hybridization with ligands, which is not evident in the electronic structure, or substantial renormalization due to e.g., spin fluctuations. Assuming that $\chi_c=5.4\times 10^{-3}$ mol^{-1} and $\chi_{ab}=3.8\times 10^{-3}$ mol^{-1} at 1.8 K are spin susceptibilities (i.e., assuming that the diamagnetic and van Vleck contributions are small), we may estimate the Wilson ratio $R_W = \pi^2 k_B^2 \chi_{\text{spin}}/(3\mu_B^2\gamma)$. This gives $R_W\sim 7$ from χ_{ab} and ~10 from χ_c. These values well exceed unity for a free-electron system and are indicative of enhanced magnetic behavior. There are several possible reasons for high R_W: one is that actual low-temperature spin susceptibility is much smaller than the total susceptibility, e.g., due to a strong orbital contribution. Another source of enhancement can be strong Coulomb correlations, which often result in Wilson ratios intermediate between 1.5 and 2.0. However, the large value that we find, which is an order of magnitude higher, is best explained as indicating that the system is close to ferromagnetism. Combined with the high R_W, we find a normal Kadowaki-Woods ratio A/γ^2. In particular, for $BaCo_2As_2$ in-plane transport we obtain $A_{ab}/\gamma^2=0.1\times 10^{-5}$ $\mu\Omega$ cm/(mJ/mol K)^2. This is comparable to the value for the nearly two-dimensional Fermi liquid, Sr_2RuO_4, smaller than the typical value of 10^{-5} $\mu\Omega$ cm/(mJ/mol k)^2 for heavy Fermions, and significantly smaller than the values found in correlated oxides with frustration or other very strong scattering such as LiV_2O_4 or $La_{1.7}Sr_{0.3}CuO_4$.[16]

Electronic structure calculations were performed using the general potential linearized augmented plane-wave (LAPW) method with local orbitals,[17,18] similar to those reported previously for $BaFe_2As_2$.[19] The calculations used LAPW sphere radii of $2.2a_0$, $2.1a_0$, and $2.1a_0$ for Ba, Co and As, respectively, and were done within the local-density approximation (LDA) with reported lattice parameters of $a=3.958$ Å, and $c=12.67$ Å.[15] The As internal coordinate z_{As} was obtained by energy minimization as $z_{\text{As}}=0.345\,28$. This value is somewhat smaller than the value that we obtained by x-ray refinement of $z_{\text{As}}=0.3515$ (5). The discrepancy between the calculated and experimental values of the As height is in the same direction as in the superconducting Fe-based phases, but is less severe. For example, the calculated value[19] for tetragonal $BaFe_2As_2$ obtained in the same way is $z_{\text{As}}=0.342$ as compared to the experimental value of $z_{\text{As}}=0.3545$ (Ref. 20), yielding a twice larger discrepancy. The discrepancy is also roughly twice larger for the Fe-chalcogenide superconductors.[21] In the Fe-based materials this discrepancy is thought to be associated with magnetism, and in particular strong spin fluctuations.[22] The significant, though smaller, deviation in the present compound may therefore also be an indication of effects of spin fluctuations.

The calculated electronic density of states and Fermi surface for the calculated LDA z_{As} are shown in Figs. 4 and 5. The DOS is rather similar to that of the Fe compounds with the exception of the position of the Fermi energy. In particular, it shows only modest covalency between Co and As, and has a pseudogap at an electron count of six d electrons per Co. The extra d electron in Co^{2+} relative to Fe^{2+} shifts E_F upwards into a region of high DOS. The Fermi surface is large and multisheeted, as shown in Fig. 5. The calculated Fermi surface has both two and three dimensional sheets, and in particular is more three dimensional than might be

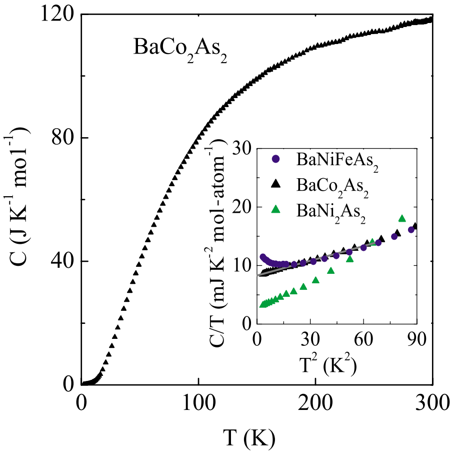

FIG. 3. (Color online) Temperature dependence of the specific heat of $BaCo_2As_2$. The inset is C/T vs T^2 and a linear fit to the data below ~7 K compared with data for $BaFeNiAs_2$ and $BaNi_2As_2$.

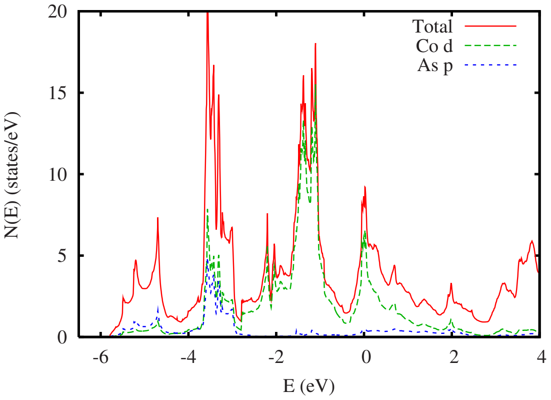

FIG. 4. (Color online) LDA non-spin-polarized electronic density of states of $BaCo_2As_2$ on a per f.u. basis. The projections shown are onto the LAPW spheres.

expected based on the anisotropy of the measured resistivity. Reconciling the Fermi surface with the transport data would require scattering that depends on the particular Fermi surface sheet, as may occur, for example, from spin fluctuations with a large anisotropy or due to strong band dependence of the electron-phonon scattering. The main As contributions to the DOS are between −6 and −3 eV relative to E_F, corresponding to stable As^{3-} and Co^{2+}. The value at the Fermi energy is $N(E_F)=8.5\ \text{eV}^{-1}$ on a per f.u. (two Co atoms) both spins basis. Comparing with the measured specific heat implies a mass renormalization of ~2, similar to the Fe-based superconductors. As shown in the inset of Fig. 3, our measured value for $BaNi_2As_2$ is $\gamma=15\ \text{mJ}/(\text{mol K}^2)$, as compared with a bare value from $N(E_F)$ of $8.9\ \text{mJ}/(\text{mol K}^2)$. This yields an enhancement factor of $(1+\lambda)=1.7$, consistent with the value of the electron-phonon $\lambda=0.76$ obtained from first-principles calculations for that compound.[12]

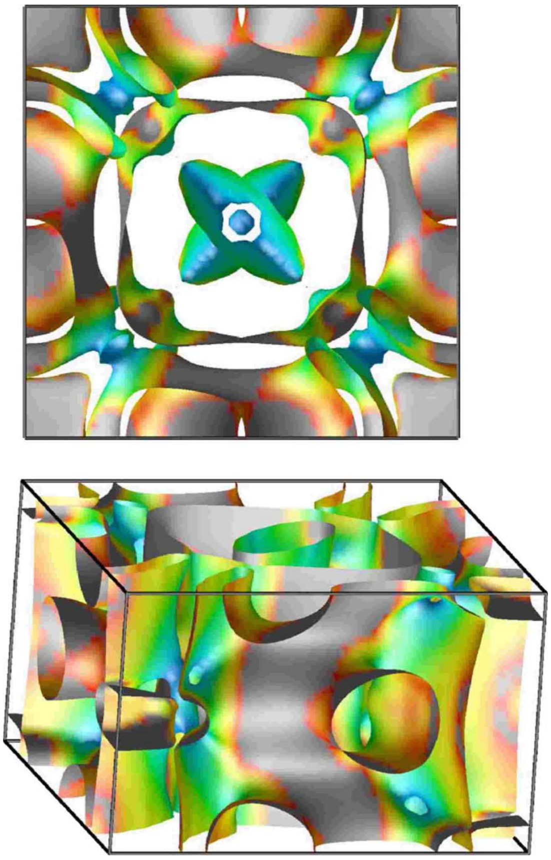

FIG. 5. (Color online) LDA non-spin-polarized Fermi surface of $BaCo_2As_2$ shaded by velocity; blue (light gray) is low velocity. The corners are Γ and M (0,0,1/2) points in the body-centered tetragonal zone.

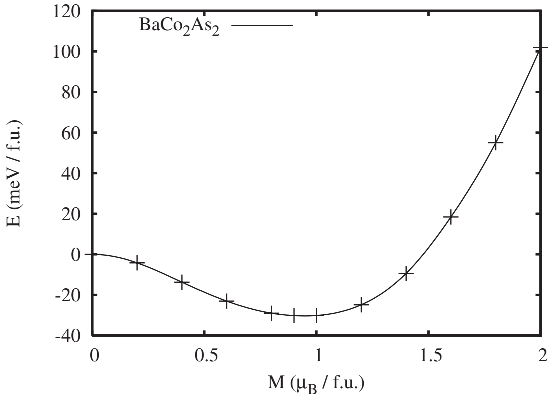

FIG. 6. LDA fixed spin moment energy as a function of constrained moment for $BaCo_2As_2$.

The physics, however, appears different in $BaCo_2As_2$ from that in $BaNi_2As_2$. First of all, the susceptibility implied by the magnetization measurements is enhanced over the Pauli susceptibility from the LDA density of states, $\chi_0=2.75\times10^{-4}$ emu/mol by a factor of ~15 (depending on direction) yielding a high Wilson ratio with implied nearness to ferromagnetism. Furthermore, the nonrenormalized LDA $N(E_F)$ is already large enough to lead to a mean-field Stoner instability toward ferromagnetism. In fact, contrary to experiment we find a stable ferromagnetic ground state in the LDA, with spin moment $0.94\mu_B/\text{f.u.}$ $(0.42\mu_B/\text{Co})$ and energy 32 meV/f.u. lower than the non-spin-polarized solution. The total energy as a function of constrained moment is shown in Fig. 6. We also searched for an antiferromagnetic solution with a checkerboard in-plane arrangement where all nearest-neighbor Co bonds are antiferromagnetic. However, we did not find a stable antiferromagnetic state of this type. This indicates that the stability of Co moments depends on the particular magnetic order and therefore that the magnetism is itinerant. Thus at the LDA level, $BaCo_2As_2$ is a weak itinerant magnet, apparently ferromagnetic in-plane, though the out-of-plane interaction may be ferromagnetic or antiferromagnetic.

While the mechanism for superconductivity of the layered Fe compounds remains to be established, there is accumulating evidence of a relationship between superconductivity and magnetism. For example, the phase diagrams show an interplay between of an itinerant spin-density wave (SDW) with superconductivity,[20,23] and density-functional calculations show a proximity to magnetism, with evidence for strong spin fluctuations.[22,24–26] Other evidence for strong magnetic effects comes from the unusual temperature dependence of the susceptibility, $\chi(T)$, which for some compounds is increasing with T up to high T,[27,28] and unusually large discrepancies between calculated and measured pnictogen crystallographic positions.[22] An important signature of the beyond mean-field spin-fluctuation effects in the Fe-based superconductors is the fact that standard density-functional calculations give much more robust magnetic moments than experiment.

Comparing our experimental and calculated results for $BaCo_2As_2$, we find a related situation. In particular, we do not find clear evidence in transport or magnetization data for a magnetic ordering (there is a change in behavior of the magnetization at ~ 60 K but the susceptibility continues increasing below this temperature, and we do not find any hysteresis). The implication is that the LDA yields a more magnetic state than experiment. This generally occurs in materials near a magnetic quantum critical point, where ordering is suppressed by quantum fluctuations in the order parameter (i.e., spin fluctuations). Examples of this behavior include the weak itinerant ferromagnets $ZrZn_2$, Ni_3Al, and the highly renormalized paramagnets Ni_3Ga and $Sr_3Ru_2O_7$,[29–33] although the renormalizations in those materials are apparently stronger than in our measurements for $BaCo_2As_2$.

Further information comes from our single-crystal measurements for $BaFeNiAs_2$, which was prepared in a similar way to $BaCo_2As_2$, using a near equal atomic mixture of Fe and Ni to obtain approximately the same average d electron count as $BaCo_2As_2$. The single crystals of $BaFeNiAs_2$ were grown using a procedure similar to that described above for $BaCo_2As_2$. The lattice parameters of $BaFeNiAs_2$ are $a=4.0002(1)$ Å, and $c=12.6767(3)$ Å, in the $ThCr_2Si_2$ structure. The measured specific heat γ (Fig. 3) is remarkably similar to those for $BaCo_2As_2$. Therefore, at least for these properties, which include the renormalization, the material behaves as a virtual crystal, meaning that the alloy of Fe and Ni behaves in many respects as if it were a true pure compound of the element with the average atomic number (i.e., Co for an equal mixture). In this way, scattering is not strong enough to alter the basic electronic structure, a fact that may be of importance in understanding why superconductivity in the $BaFe_2As_2$ is robust against the disorder introduced by alloying with Co or Ni.

Our results show no evidence of superconductivity in $BaCo_2As_2$. This is as might be anticipated. While the electronic structure is formed in a similar fashion to those of $BaFe_2As_2$ and superconducting $Ba(Fe_{1-x}Co_x)_2As_2$ the electron count is higher leading to a very different electronic structure at E_F. In particular, the topology of the Fermi surface is very different. Furthermore, even though both the Fe and Co compounds are near itinerant magnetism, the nature of the magnetism is very different. The Fe compounds are near a SDW associated with Fermi-surface nesting, while $BaCo_2As_2$ is near ferromagnetism. Unlike spin fluctuations associated with an SDW, which are pairing for, e.g., singlet $s_\pm$ superconductivity, ferromagnetic spin fluctuations are strongly pair breaking for any singlet superconductivity, including electron-phonon superconductivity. Considering the present results for the electronic structure, one possibility for producing high-temperature superconductivity based on cobalt would be to lower the electron count to move the material away from ferromagnetism and to produce a Fermi surface similar to the Fe-based materials. In this regard, Co^{3+} is a chemically stable valence for Co (as in e.g., $LaCoO_3$ and $LiCoO_2$). Furthermore, KCo_2As_2 is a known $ThCr_2Si_2$ structure compound, which might conceivably be the basis of a Co superconductor if the electron count could be further lowered, e.g., through K vacancies or alloying of As with a group IV element.

To summarize, we find from comparison of experimental data on single crystals and LDA calculations that $BaCo_2As_2$ is a substantially renormalized metal near a magnetic quantum critical point, probably of ferromagnetic character. It will be of interest to tune the proximity to the critical point. One interesting possibility would be to alloy on the Ba site with a magnetic element, e.g., Eu, which may favor formation of a magnetically ordered state.

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