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Magnetic and structural transitions in layered iron arsenide systems: AFe$_2$As$_2$ versus RFeAsO

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Resistivity, specific-heat, and magnetic-susceptibility measurements performed on $SrFe_2As_2$ samples evidence a behavior very similar to that observed in LaFeAsO and $BaFe_2As_2$, with the difference being that the formation of the spin-density wave and the lattice deformation occur in a pronounced first-order transition at $T_0=205$ K. Comparing further data evidences that the Fe magnetism is stronger in $SrFe_2As_2$ and in $EuFe_2As_2$ than in the other layered FeAs systems investigated up to now. Full potential local-density approximation band-structure calculations confirm the large similarity between the compounds, especially for the relevant low energy Fe 3d states. The relation between structural details and magnetic order is analyzed.

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The discovery of superconductivity in doped LaFeAsO (Ref. 1) and the subsequent raising of the superconducting (SC) transition temperature T_c to 56 K (Refs. 2–5) initiated a surge of interest in layered FeAs systems. Undoped RFeAsO compounds (R=La-Gd) present a structural transition at $T_0 \sim 150$ K followed by the formation of a spin-density wave (SDW) at a slightly lower temperature $T_N \sim 140$ K.[6,7] Electron or hole doping by substituting O by F,[5], substituting R by a tetravalent or divalent cation,[8,9] or by reducing the O content[10] leads to the suppression of the SDW and to the onset of superconductivity. This connection between a vanishing magnetic transition and the simultaneous formation of a SC state is reminiscent of the behavior in the cuprates and in the heavy fermion systems. It therefore suggests the SC state in these doped RFeAsO systems to be of unconventional nature as well. While this has to be confirmed by further studies, there seems to be a general belief that the intriguing properties of these compounds are connected with very peculiar properties of the FeAs layers.

In this Rapid Communication we show that the AFe$_2$As$_2$ compounds, where A stands for a divalent cation such as Sr, Eu, or Ba, present the same unusual features as the RFeAsO compounds because of almost identical FeAs layers leading to almost identical electronic density of states (DOS) at the Fermi level. For this purpose, we review previous investigations of the magnetic properties of the AFe$_2$As$_2$ compounds, which already evidence a clear similarity to the RFeAsO ones. We then present results on $SrFe_2As_2$ that confirm this analogy. Finally, we perform band-structure calculations that reveal the electronic states, especially the relevant low energy Fe 3d states, to be nearly identical in both types of compounds. Furthermore, our results show that the AFe$_2$As$_2$ compounds are not just duplicates of the RFeAsO ones but they show features that lead to a different insight into the physics of the layered FeAs systems. Thus, we observe in $SrFe_2As_2$ only one extremely sharp first-order transition at $T_0=T_N=205$ K, where both the antiferromagnetic (AFM) ordering and the lattice distortion occur, in contrast to the two broad second-order transitions reported for RFeAsO. This result has strong implications for the understanding of the magnetism in the FeAs layers. Furthermore, $SrFe_2As_2$ offers a unique opportunity to assess the relevance of magnetic interactions for the superconductivity in the layered FeAs systems because it presents a stronger magnetic character, as evidenced, e.g., by a larger T_0, while all other layered FeAs systems known up to now are quite similar in this aspect. If magnetism is important for the SC state, then the SC properties of doped $SrFe_2As_2$ should differ from those of doped $BaFe_2As_2$ or RFeAsO compounds. While finalizing our investigation Rotter *et al.* submitted a paper on $BaFe_2As_2$.[11] They suggest the presence of a second-order phase transition at 140 K where both SDW and lattice distortion set in. Ni *et al.*[12] reported similar results on $BaFe_2As_2$, together with a SC transition in K doped samples.

The tetragonal ZrCuSiAs structure type in which the RFeAsO compounds crystallize[13] results in a square Fe lattice with As in the center of the square but being alternately shifted above and below the Fe plane. It is well known that the $ThCr_2Si_2$ structure type presents a very similar arrangement of the transition metal and p element. Thus it was natural to look for appropriate candidates within the huge amount of compounds crystallizing in this structure type. In a very primitive approach, the RFeAsO compounds can be rationalized as a stack of alternating $(Fe_2As_2)^{2-}$ and $(R_2O_2)^{2+}$ layers. Exchanging the $(R_2O_2)^{2+}$ layer by a layer with a single large atom A leads to the $ThCr_2Si_2$ structure type. In order to keep the same electron counts as in the RFeAsO materials, A has to be a divalent atom. Therefore, appropriate candidates are $A^{2+}Fe_2As_2$ compounds. Three of the possible candidates have already been investigated. Pfisterer and Nagorsen[14,15] have reported the synthesis, the structure, as well as preliminary susceptibility data of $SrFe_2As_2$ and $BaFe_2As_2$. From their susceptibility data they concluded the occurrence of a magnetic phase transition around 200 and 130 K, respectively, and suggested it to be an AFM one. Later on, Raffius *et al.*[16] presented a more detailed investigation of $EuFe_2As_2$, which unambiguously demonstrated AFM ordering of Fe at 200 K (as well as AFM ordering of Eu^{2+} at 19 K). From the analysis of the Mössbauer data, which revealed, e.g., a very small hyperfine field, they concluded the Fe magnetism to be itinerant. Interestingly, they reported in the same paper temperature-dependent Mössbauer spectra of LaFeAs, which was later corrected to be LaFeAsO, and inferred that in this compound Fe also presents itinerant magnetism and orders magnetically at 139 K.[17] Thus, the presence of itinerant magnetism in LaFeAsO as well as the magnetic ordering at around 134 K is not an original discovery in the very recent publications but was already established by a microscopic method 15 yrs ago. In the context of the present paper, it is more important to notice that the Fe-Mössbauer data in

$EuFe_2As_2$ (where Eu was proven to be divalent) are quite similar to those in LaFeAsO with only a slightly larger (but still very small) hyperfine field. This similarity, as well as some resemblance between the susceptibility data of $SrFe_2As_2$ with those of LaFeAsO, gave evidence for a strong analogy between the magnetism in $A^{2+}Fe_2As_2$ and that in LaFeAsO.

We synthesized polycrystalline $SrFe_2As_2$ samples by heating a stoichiometric mixture of Sr (3.5*N*), Fe (4*N*), and As (7*N*) in an Al_2O_3 crucible, sealed under an inert atmosphere (Ar 6.0) inside an evacuated quartz tube. In a first step, the elements were heated very slowly to 950 °C and kept at this temperature for 10 h; subsequently, the mixture was cooled down to room temperature. The reaction product was ground and pelletized, and, for a second heating step, sealed inside a Ta crucible and sintered at 1100 °C, again for 10 h. The resulting pellet with a metallic luster was found to be unstable in air and, therefore, was kept under an inert atmosphere. The powder of this pellet was characterized by x-ray diffraction (XRD) recorded on a STOE diffractometer in transmission mode using monochromatic Cu-K_α radiation ($\lambda = 1.5406$ Å). The resulting XRD pattern can be well indexed on the basis of a tetragonal $ThCr_2Si_2$-structure type and did not reveal any foreign phase peak. The lattice parameters $a = 3.924(3)$ Å and $c = 12.38(1)$ Å, refined by simple least square fitting, were found to be in good agreement with the reported structure data.[14] The dc susceptibility $\chi(T)$ was measured in a commercial quantum design (QD) magnetic property measurement system (MPMS). ac resistivity $\rho(T)$ measurements down to 1.8 K were carried out in a standard four-probe geometry using a QD physical property measurement system (PPMS). The PPMS was also used to determine the specific heat $C(T)$ with a standard heat-pulse relaxation technique. To gain deeper insight into the electronic structure of the investigated compound on a microscopic level, we performed density-functional band-structure calculations within the local (spin) density approximation [L(S)DA]. Using the experimental structural parameters,[6,11,14,15] we applied the full-potential local-orbital (FPLO) code[18] (version 7.00–28) with the Perdew-Wang exchange-correlation potential[19] and a well converged k mesh of 24^3 points for the Brillouin zone.

The most prominent features are observed in the resistivity and in the specific heat, while the temperature dependence of the susceptibility is rather weak. Below 300 K, $\rho(T)$ decreases slightly with temperature T (Fig. 1) and thus evidences metallic behavior, although the absolute value at 300 K is somewhat larger than in a classical metal (but well below the values observed in typical LaFeAsO samples). Moreover, the slope $\partial\rho(T)/\partial T$ is comparatively small. At $T_0 = 205$ K, we observe a sharp steplike drop in $\rho(T)$ with a step size $\Delta\rho/\rho_{210\ \mathrm{K}} \sim 6\%$, followed by a continuous decrease by more than one order of magnitude down to 1.8 K. This results in a resistivity ratio (RR) of about $\rho_{300\ \mathrm{K}}/\rho_{1.8\ \mathrm{K}} = 32$, which is much larger than that observed in LaFeAsO (Ref. 7) or in $BaFe_2As_2$.[11] Since such a strong decrease can hardly be attributed to the vanishing of spin disorder scattering, it indicates pronounced changes of the electronic states at the Fermi level.

In contrast, $\chi(T)$ increases only slightly with decreasing temperature below 300 K (inset of Fig. 1), the increase being more pronounced at small applied fields, which indicates this increase to be due to paramagnetic impurities or magnetic foreign phases. The susceptibility above T_0 is compatible with an enhanced Pauli susceptibility. At T_0, $\chi(T)$ also presents a steplike decrease but there is no further decrease at lower temperatures. The size of the step at T_0, $\Delta\chi = 1.1 \times 10^{-9}$ m^3/mol, corresponds to a relative change $\Delta\chi/\chi_{210\ \mathrm{K}} \sim 5\%$, quite similar to the relative size of the step in $\rho(T)$ of 6%. In an itinerant scenario, it would suggest a decrease in the density of states at the Fermi level by just 5%. The specific heat $C(T)$ (Fig. 2) provides very clear evidence for a pronounced first-order transition at T_0. On the top of a monotonously increasing $C(T)$, as expected from the phonon contribution, we found a very sharp and huge peak centered at $T_0 = 205$ K with a half width at half maximum of less than 0.4 K. For tracing such a sharp peak, instead of determining a single $C(T)$ value by fitting the whole relaxation curve with an exponential function, it is more appropriate to calculate a continuous $C(T)$ curve from the time derivative of the relaxation curve directly.[20] The relaxation

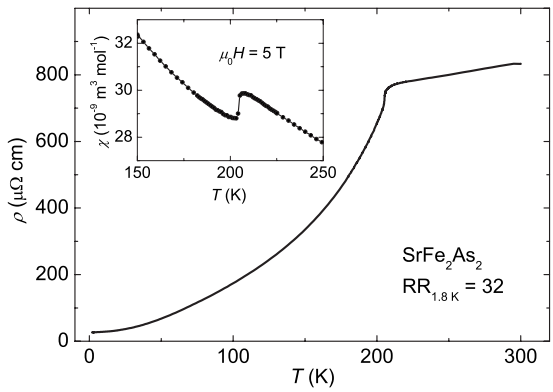

FIG. 1. Temperature dependence of the electrical resistivity $\rho(T)$ of $SrFe_2As_2$. A steplike decrease marks the first-order phase transition at $T_0 = 205$ K. The magnetic susceptibility $\chi(T)$ measured at $\mu_0 H = 5$ T is shown in the inset.

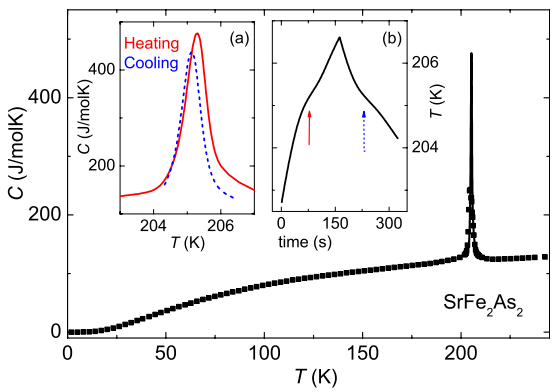

FIG. 2. (Color online) Specific heat of $SrFe_2As_2$ plotted as C versus T. A sharp first-order type anomaly is visible at $T_0 = 205$ K. This anomaly is enlarged in inset (a), determined from a heating (solid line) and a cooling (dashed line) curve in a relaxation-time measurement, shown in inset (b). The arrests in the temperature-time relaxation curve due to latent heat are depicted by arrows.

curve across the transition is shown in the right inset of Fig. 2 while $C(T)$ determined directly from the slope is shown in the left inset. One immediately notices the shoulders (arrows) in the relaxation curve, which are direct evidence for a thermal arrest and thus for a first-order transition (see, e.g., Ref. 20). Also the hysteresis between $C(T)$ determined from the cooling and the heating parts of the relaxation curve indicate a first-order transition. From the area under the peak in $C(T)$, one can estimate the latent heat ΔH as well as the entropy ΔS connected with the transition. They amount to $\Delta H \sim 200$ J/mol and $\Delta S \sim 1$ J/mol K. This small value of ΔS can be taken as evidence for an itinerant Fe moment. Muon spin-relaxation and XRD measurements confirm that the formation of the SDW and the lattice deformation occurs simultaneously at T_0, which will be presented in a forthcoming paper.[21]

Our experimental results confirm the presence of a single transition at $T_0 = 205$ K in $SrFe_2As_2$, and show that the overall behavior of the susceptibility and resistivity of $SrFe_2As_2$ is quite similar to that of the undoped *R*FeAsO compounds and $BaFe_2As_2$. This suggests that the underlying physics is the same. However, a more detailed comparison indicates that $BaFe_2As_2$ is almost identical to the *R*FeAsO series while the replacement of Ba by the smaller Sr or Eu^{2+} enhances the magnetic character of the FeAs layers. This is obvious from the ordering temperature, which increases from $T_0 \sim 150$ K in the former ones to $T_0 \sim 200$ K in the latter ones. $EuFe_2As_2$ and $SrFe_2As_2$ being almost identical is not surprising since Sr has almost the same ionic radius as Eu^{2+}, and is often used as a nonmagnetic reference for Eu^{2+} compounds. The increase in the ordering temperatures is accompanied by an increase in the ordered Fe moment, as evidenced by the increase in the hyperfine field B_{hf} determined in Fe-Mössbauer experiments from $B_{hf} \sim 5.1 \pm 0.2$ T in LaFeAsO (Refs. 7 and 16) and $BaFe_2As_2$ (Ref. 11) to $B_{hf} = 8.5$ T in $EuFe_2As_2$.[16] Furthermore, the value of the Pauli-like susceptibility above the transition also increases from $\sim 5 \times 10^{-9}$ m^3/mol-Fe in LaFeAsO (Ref. 7) and $\sim 6 \times 10^{-9}$ m^3/mol-Fe in $BaFe_2As_2$ (Ref. 11) to $\sim 13 \times 10^{-9}$ m^3/mol-Fe in $SrFe_2As_2$. This increase in the magnetic character of $EuFe_2As_2$ and $SrFe_2As_2$ cannot be easily related to a change in the structural parameters. The lattice parameter a decreases from $BaFe_2As_2$ [$a = 3.9625$ Å (Ref. 11)] to $SrFe_2As_2$ ($a = 3.924$ Å) and $EuFe_2As_2$ [$a = 3.911$ Å (Ref. 22)] but this reduction is smaller than that within the *R*FeAsO series. There a decreases from 4.0355 Å in LaFeAsO (Ref. 1) to 3.9151 Å in GdFeAsO (Ref. 9) without increasing T_0. Also the buckling of the FeAs layers does not seem to change strongly as deduced from the distance of the As atoms to the Fe plane, which within the present accuracy of the reported data stays around 1.40 ± 0.05 Å. Thus the increase in T_0 by 35% in $SrFe_2As_2$ and $EuFe_2As_2$ compared to the other compounds has to be related to more subtle changes in the electronic properties.

The calculated electronic DOS for LaFeAsO and AFe_2As_2 ($A = Sr, Ba$) is shown in Fig. 3. On a first glance, the total DOS of the AFe_2As_2 systems is basically identical, evidencing the strong analogy between the two compounds even on small energy scales. However, also the LaFeAsO system exhibits a very similar electronic structure, especially in the

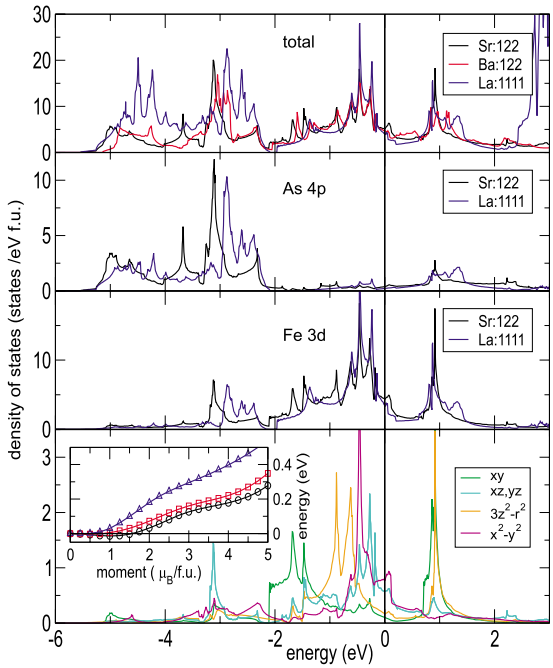

FIG. 3. (Color online) Total and partial DOSs for $SrFe_2As_2$ (Sr:122), $BaFe_2As_2$ (Ba:122), and LaFeAsO (La:1111). The bottom panel shows the orbital resolved Fe 3*d* DOS for $SrFe_2As_2$. The inset provides the FSM results for the three compounds; the symbols present the calculated points.

relevant low energy region that is dominated by Fe 3*d* states for all three compounds. The main differences appear in the region below −4 eV due to O 2*p* states, and above 2.5 eV due to the La 4*f* states that are naturally absent in the other two systems. Smaller differences between the AFe_2As_2 compounds and the LaFeAsO system are observed in the region between −4 and −2 eV where the main contribution is due to the As 4*p*-Fe 3*d* hybrid states. For LaFeAsO, these states are shifted to higher energies by about 300 meV (see Fig. 3). A surprisingly close similarity of all three systems is observed for the Fe 3*d* states close to the Fermi level where these states provide the predominant contribution to the total DOS. This close similarity even holds for the orbital resolved Fe 3*d* DOS (shown for $SrFe_2As_2$ in the bottom panel of Fig. 3). These results suggest that all three systems should behave very alike with respect to their physical properties, including the response upon doping, pressure, and other external parameters.

However, a closer analysis of the orbital resolved Fe 3*d* DOS yields a strong dependency of the occupation of the Fe $3d_{x^2-y^2}$ orbital on structural details such as the exact As z position. These small differences influence crucially the magnetic behavior: Whereas we find a magnetic ground state for all three compounds using the experimental As position, we find a nonmagnetic state with optimized As z parameters[23] that results in slightly smaller (~0.08 Å) Fe-As distances. The occupation of the Fe $3d_{x^2-y^2}$ orbital increases with decreasing Fe-As distances because of a downshift of the related band near Γ. This shift is connected to a considerable number of states because this band is almost dispersionless along [001]. If this band falls below the Fermi

level along [001], the magnetic state breaks down.

For the experimental structure, we find an antiferromagnetic ground state for all three systems with a Fe moment of about $1.7\mu_B$. Analyzing fixed spin moment (FSM) calculations (inset of Fig. 3), we also find evidence for a ferromagnetic (FM) instability from minima in the FSM curves. These minima ($m_{Sr}=1.02\mu_B$, $m_{Ba}=0.50\mu_B$, $m_{La}=0.25\mu_B$) coincide with the FM moments obtained in unconstrained calculations. The larger size of the magnetic moment and the energy dependence of the FSM curve support the experimental observation of stronger magnetic character of $SrFe_2As_2$. Interestingly, for all compounds, the FSM curves show a second anomaly as a reminisce of the AFM state. In addition, we investigated the structural stability with respect to the orthorhombic splitting for $BaFe_2As_2$ and $SrFe_2As_2$ [using the splitting ratio reported for $BaFe_2As_2$ (Ref. 11)], calculating the respective total energies. For both compounds, the orthorhombic solution is more stable. The calculated energy differences compare quite well with the measured latent heat ΔH of 200 J/mol.

In summary, we prepared polycrystalline $SrFe_2As_2$ samples and measured the resistivity, magnetic susceptibility, and specific heat. All the results evidence a very pronounced first-order transition at $T_0=205$ K with a width of less than 1 K, in contrast to the broader, second-order-like transitions observed in the *R*FeAsO series and in $BaFe_2As_2$. The resistivity decreases strongly below T_0, leading to a resistivity ratio of 32 at 1.8 K, which is much larger than that found in the other compounds. In contrast, the susceptibility is almost T independent and presents only a steplike decrease at T_0. This behavior is very similar to that reported for the *R*FeAsO compounds and for $BaFe_2As_2$, which indicates that the underlying physics is the same. However, the larger ordering temperature in $SrFe_2As_2$ and $EuFe_2As_2$, the larger value of the Pauli-like susceptibility above T_0 in $SrFe_2As_2$, as well as the larger Fe hyperfine field observed in Mössbauer experiments indicate a stronger magnetic character in these two compounds. The local-density approximation (LDA) band-structure calculations evidence a pronounced similarity between the *R*FeAsO and the $A^{2+}Fe_2As_2$ compounds, especially for the relevant low energy Fe $3d$ states. They confirm the magnetic order to be more stable in $SrFe_2As_2$ than in $BaFe_2As_2$ or in LaFeAsO. A closer analysis reveals a strong dependence of the occupation of the Fe $3d_{x^2-y^2}$ orbitals on structural details such as the exact As z position with a large impact on the Fe magnetism. Because of its stronger magnetic character, including a larger T_0, $SrFe_2As_2$ likely offers a unique possibility for assessing the relevance of magnetic interactions for the superconductivity in layered FeAs systems.

After submission we recognize the report of a first-order transition at T_0 in $CaFe_2As_2$.[24]

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