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# Strong coupling between magnetic and structural order parameters in $SrFe_2As_2$

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X-ray and muon spin-relaxation experiments performed on $SrFe_2As_2$ polycrystals confirm a sharp first-order transition at $T_0=205$ K corresponding to an orthorhombic phase distortion and to a commensurate antiferromagnetic Fe ordering with a larger distortion and larger size of the ordered moment than reported for $BaFe_2As_2$. The structural and the magnetic order parameters present a remarkable similarity in their temperature dependence from $T_0$ down to low temperatures, showing that both phenomena are intimately connected. Accordingly, the size of the ordered Fe moments scales with the lattice distortion when going from $SrFe_2As_2$ to $BaFe_2As_2$. Full-potential band-structure calculations confirm that the columnar magnetic order with propagation vector (1,0,1) and the orthorhombic lattice distortion are intrinsically tied to each other.

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Compounds with FeAs layers have recently attracted considerable interest because they present an intriguing magnetic and structural transition, which gets suppressed upon doping resulting in the appearance of high-temperature superconductivity (SC). This behavior was observed in the RFeAsO series of compounds (R=La-Gd) (Refs. 1–5) and more recently in the $AFe_2As_2$ class of materials (A=Ba, Sr).[6–10] The onset of SC at the disappearance of a magnetic ordered state is reminiscent of the behavior in the cuprates and in the heavy fermion systems and, therefore, suggests the SC state in these doped layered FeAs systems to be of unconventional nature, too. 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. While the occurrence of magnetic order in LaFeAsO and in the $AFe_2As_2$ compounds has been reported already more than 15 years ago,[11,12] the observation of the lattice deformation is quite recent.[3,5,6,13] The interaction between both phenomena is a very interesting problem on its own. A thorough understanding of these two phenomena, their mutual relation, and how they get suppressed under doping is likely a prerequisite to get a deeper insight into the origin and the nature of the superconducting state. In the RFeAsO compounds, the formation of the spin-density wave (SDW) seems to occur in a second-order transition at a slightly lower temperature $T_N \approx 140$ K than the structural transition at $T_0=150$ K.[3,4] For $BaFe_2As_2$, the report by Rotter *et al.*[6] suggested both ordering phenomena to occur simultaneously at a second-order transition at $T_0=140$ K. Shortly later, Huang *et al.*[14] claimed the structural distortion to be first order while the magnetic order sets in continuously once the structural distortion is completed. Thus, the present picture for both the RFeAsO and $BaFe_2As_2$ systems suggests that the structural distortion has to be completed before the antiferromagnetic (AF) order can form, and that the two order parameters are not directly connected. For $SrFe_2As_2$, we recently showed that a high-quality sample presents a very sharp first-order transition at $T_0=205$ K, without any evidence for a second transition.[8] In the present Rapid Communication we report a precise study of the evolution of the magnetic and of the structural order parameter in this compound by combining temperature-dependent muon spin-resonance and x-ray diffraction measurements with bulk susceptibility, resistivity, specific heat, as well as preliminary Mössbauer and neutron-scattering data. Our results demonstrate that in $SrFe_2As_2$, the formation of the SDW and the lattice distortion are intimately coupled. Comparison with results reported for $BaFe_2As_2$ also supports a strong connection between both order parameters.

The sample preparation and characterization have been described in detail in our previous paper.[8] The main aspect of our synthesis process is to allow for a slow and progressive reaction of a stoichiometric amount of pure elements by increasing slowly and stepwise the reaction temperature up to 1150 °C. This results in polycrystalline samples with an excellent resistivity ratio $RR_{1.8K}=32$, better than in most of the reported single crystals. Susceptibility $\chi(T)$, specific heat $C(T)$, and resistivity $\rho(T)$ measurements were carried out using standard techniques in commercial equipments physical property measurement system and magnetic property measurement system of Quantum Design. Temperature-dependent x-ray powder pattern were obtained using an imaging plate Guinier Camera HUBER G670 (Co-$K_\alpha$ radiation) equipped with a closed cycle cryostat. Zero-field muon spin-relaxation ($\mu$SR) experiments were performed between 1.6 and 300 K using the General Purpose Surface-Muon Instrument at the Paul Scherrer Institute. To gain deeper insight into the relation of magnetism and the orthorhombic distortion in $AFe_2As_2$ on a microscopic level, we performed density functional band-structure calculations within the local (spin) density approximation. Using the experimental structural parameters of the tetragonal cell[11,12,15] as a starting point, we applied the full-potential local-orbital (FPLO) code[16] (version 7.00–28) in both scalar-relativistic and fully relativistic versions, respectively, with the Perdew-Wang exchange correlation potential.[17] A well-converged $k$ mesh of at least $18^3$ points within the Brillouin zone of the larger orthorhombic cell has been used.

 

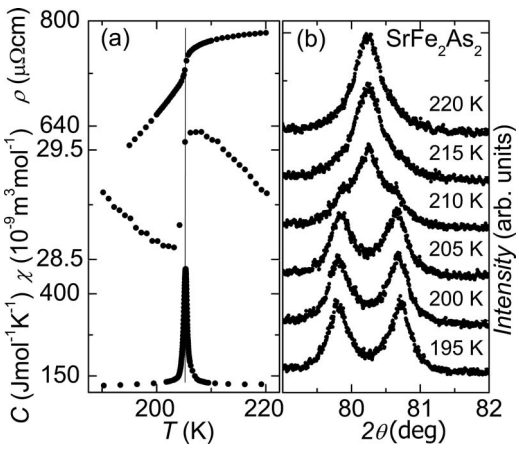


FIG. 1. (a) Resistivity, susceptibility, and specific heat in $SrFe_2As_2$ near the first-order transition at $T_0$=205 K. (b) Splitting of the 220 tetragonal peak into the 400 and 040 peaks of the orthorhombic structure below $T_0$.

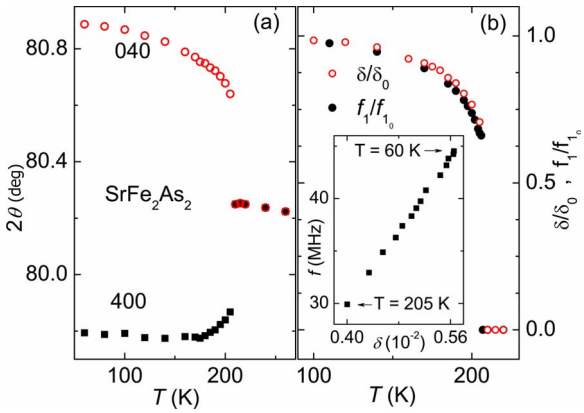


FIG. 2. (Color online) (a) $T$ dependence of the positions of the 040 and 400 peaks. (b) $T$ dependence of the lattice distortion $\delta(T)$ and of the muon precession frequency $f_1$ normalized to their saturation values at low $T$. Inset: $f_1$ versus $\delta$ with $T$ as implicit parameter.

In Fig. 1(a) we show the anomalies in $\rho(T)$, $\chi(T)$, and $C(T)$, which evidence a sharp first-order transition in our polycrystalline $SrFe_2As_2$ sample, as discussed in our previous paper.[8] While $\rho(T)$ is only weakly decreasing with temperatures between 300 and 205 K, it presents a 5% drop at $T_0$ followed by a further strong decrease to low temperatures. The susceptibility, except for a Curie-type contribution likely due to paramagnetic impurities or a small amount of foreign phases, seems to be $T$ independent above and below $T_0$, but presents also a drop of $\Delta\chi \approx 1.1 \times 10^{-9}$ m$^3$/mol at $T_0$. The specific-heat measurement shows a sharp peak at $T_0$, which was interpreted as first-order transition with a latent heat $\Delta H \approx 200$ J/mol. We shall first focus on the results of the x-ray measurements. At room temperature and down to 210 K the powder-diffraction pattern evidenced an undistorted tetragonal (TT) $ThCr_2Si_2$ structure type. In contrast, in all patterns taken at 205 K or lower temperatures, some of the Bragg peaks are well split, while others are not, demonstrating the structural distortion [Fig. 1(b)]. The pattern at 205 K and below can be well fitted with an orthorhombic (OT) unit cell ($Fmmm$) with $a_{OT}=a_{TT}\sqrt{2}(1+\delta)$ and $b_{OT}=a_{TT}\sqrt{2}(1-\delta)$ in analogy to the structure proposed for $BaFe_2As_2$ (Ref. 6) and in accordance with Ref. 13. So, $\delta$ corresponds to the order parameter of the structural phase transition. A lattice parameter fit at the lowest investigated temperature $T$ =60 K gave $a$=5.5746(4) Å, $b$=5.5130(8) Å, and $c$ =12.286(4) Å, corresponding to a saturation value of the distortion $\delta_0=0.56(1)\times 10^{-2}$ at low $T$. The evolution of $\delta$ with temperature was determined by analyzing precisely the splitting of the 400/040 Bragg peaks [Figs. 1(b) and 2(a)]. Here we included data taken upon cooling and heating the sample. We did not observe any differences between both sets of data. Between 210 and 205 K, the 220 peak of the TT high-temperature phase disappears abruptly, being replaced by the 400 and 040 peaks of the OT low-temperature phase. At 210 K, shoulders on both sides of the 220 peak indicate that a small amount of OT phase is coexisting with the TT phase, in accordance with a first-order transition. The presence of this OT phase above $T_0$ might be due to strain or defects induced by the powdering process. The distortion $\delta$ increases steplike to 70% of $\delta_0$. This is a further clear evidence for a first-order transition. However, $\delta$ continues to increase with decreasing temperatures, indicating a further strengthening of the order parameter below the transition. A comparison with the data reported previously by Yan *et al.*[13] gives strong evidence that this further increase in $\delta(T)$ below $T_0$ is an intrinsic property and not just a consequence of an imperfect sample. In general both sets of data are similar.[18] However, our results evidence a very abrupt transition from the TT to the OT phase, while the data of Ref. 13 show a large coexistence region ranging from 160 up to 198 K. This broadening of the transition, as well as the lower $T_0$ in the 122 single crystals of Ref. 13, is due to Sn incorporation. However, both the absolute value of the splitting at low $T$ and that at the transition are very similar to our results. Thus, while the transition temperature and the sharpness of the transition are quite sensitive to defects, the splittings at $T_0$ and at $T \to 0$ K, as well as the increase in $\delta(T)$ below $T_0$, are not.

Precise information on the evolution of the magnetic order parameter was obtained from $\mu$SR experiments. Muon spin relaxation is a well-established method for revealing and studying magnetic order. It probes the local field induced at the site(s) of the muon by slowly fluctuating or ordered nearby magnetic moments. For temperatures above 205 K we observe only a slow decay of the muon polarization, as expected for a nonmagnetic material. Below 205 K, well-defined and strong oscillations appear in the time dependence of the muon polarization, as shown in the inset of Fig. 3, evidencing a precession of the muon in an internal field. A Fourier analysis of the signal reveals two distinct components with very well-defined frequencies: one at $f_1$ =44 MHz corresponding to ≈70% of the signal and one at $f_2$=13 MHz corresponding to ≈30% of the signal.[19] This indicates the presence of two distinct muon sites, one being more strongly and one more weakly coupled to the Fe moments. This resembles the situation in LaFeAsO where also two components—one with a larger frequency $f_1$=23 MHz corresponding to 70% of the muons and one with a lower

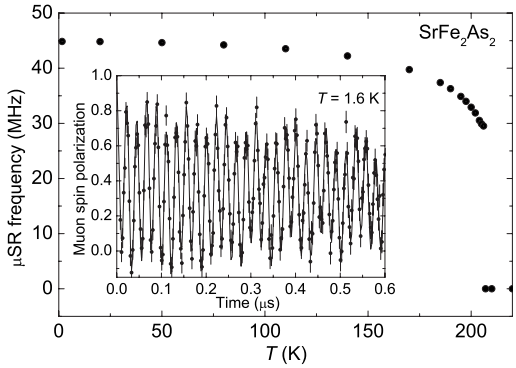


FIG. 3. Temperature dependence of the muon precession frequency $f_1$. Inset: Time dependence of the muon spin polarization at $T=1.6$ K.

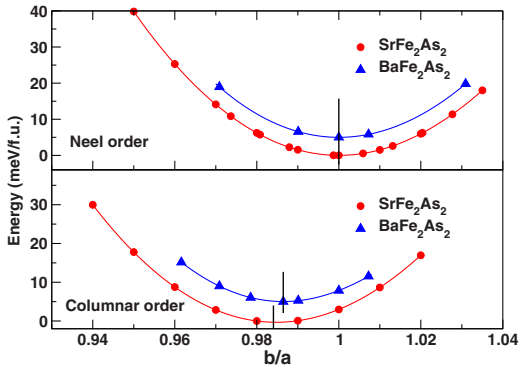


FIG. 4. (Color online) Calculated total energy versus axis ratio $b/a$ for the orthorhombic unit cell of $SrFe_2As_2$ (circles) and $BaFe_2As_2$ (triangles). The calculated data points are marked by the symbols; the lines are fourth-order polynomial fits. The minima are marked by vertical lines. The minimum of $SrFe_2As_2$ is chosen as zero energy and the $BaFe_2As_2$ curves are shifted upwards by 5 meV. The upper panel shows no distortion for a Néel order within the FeAs layers, whereas the lower panel demonstrates the orthorhombic distortion for columnar order in the FeAs layer.

frequency $f_2=3$ MHz corresponding to 30% of the muons—were observed.[4] Preliminary Fe Mössbauer experiments evidenced very well-defined hyperfine splitting at low $T$, corresponding to a hyperfine field of 8.5 T,[19] which is identical to the value reported for $EuFe_2As_2$.[12] The ratio between the respective $f_1$ frequencies in $SrFe_2As_2$ and LaFeAsO is similar to the ratio of the hyperfine field measured in Mössbauer experiments and, thus, to the ratio of the ordered Fe moments. This suggests that the muon site corresponding to $f_1$ is the same in both types of compounds and likely located within the FeAs layers, while the muon site corresponding to $f_2$ is probably in the region separating the FeAs layers, which differs between both types of compounds. The oscillations we observed in $SrFe_2As_2$ are much better defined than those reported for LaFeAsO, which is likely related to a much better crystallinity and higher homogeneity of the $AFe_2As_2$ compounds compared to the RFeAsO ones. On the other hand it indicates that the internal field at each muon site in $SrFe_2As_2$ is sharply defined, implying a well-defined long-range commensurate magnetic order. This was confirmed by neutron-scattering experiments, which revealed sharp magnetic Bragg peaks below $T_0$, similar to those reported for $BaFe_2As_2$. The higher precision of our measurement allowed to uniquely fix the magnetic structure as a columnar antiferromagnetic order with propagation vector (1,0,1) and Fe moment of $\mu_B$ oriented along the $a$ axis.[20] A neutron-scattering study on a $SrFe_2As_2$ single crystal confirmed this columnar magnetic structure with moments ordered antiferromagnetically along the large Fe-Fe distance and ferromagnetically along the short Fe-Fe distance.[21] Furthermore, the same antiferromagnetic structure was also reported for $CaFe_2As_2$.[22] In the main part of Fig. 3, we show the temperature dependence of $f_1$ in $SrFe_2As_2$. $f_1$ is proportional to the size of the ordered moment and, thus, to the magnetic order parameter. In contrast to LaFeAsO, where $f_1$ is increasing continuously below a second-order transition at $T_N \approx 134$ K, we observe in $SrFe_2As_2$ at 205 K a sharp steplike increase in $f_1$ to 66% of its saturation value at low $T$ ($f_{1_0}=44$ MHz). This is again an indication for a first-order transition. However, as already noticed for the $T$ dependence of the lattice distortion $\delta$, also the magnetic order parameter further increases below $T_0$ with decreasing $T$. We compare in Fig. 2(b) the $T$ dependence of $\delta(T)$ and $f_1(T)$ normalized to their saturation values at low $T$. The $T$ dependencies are identical within the accuracy of the experiments. In the inset of Fig. 2(b), $f_1$ is plotted as a function of $\delta(T)$ with $T$ as an implicit parameter, clearly evidencing a linear dependence between both parameters. A straight line drawn through the data points almost extrapolates to $f_1=\delta=0$. This demonstrates that both order parameters are intimately coupled to each other. A strong coupling between the magnetic and the structural order parameter, as well as a clear evidence for a first-order transition, was nicely demonstrated in the neutron studies on $CaFe_2As_2$ of Goldman.[22] All these results indicate that the smooth increase in the intensity of the neutron Bragg peaks reported for $BaFe_2As_2$ by Ref. 14 do not reflect the real increase in the intensity of the ordered moment maybe because of problems due to weak intensity and reduced coherence length.

To elucidate the role of various possible magnetic orderings for the OT distortion of the crystal structure for $SrFe_2As_2$ and the related Ba compound, we performed band-structure calculations for various spin configurations within the FeAs layers. Starting from different initial ordering patterns, we obtained self-consistent solutions for (i) nonmagnetic, (ii) ferromagnetic, (iii) Néel ordered, and (iv) columnar ordered FeAs layers. For both systems the lowest energy was found for the columnar ordered state. Starting from the experimental structural parameters for the TT unit cells we varied the axis ratio $b/a$, keeping the other parameters and the cell volume constant. The resulting curves for the Néel ordered and columnar ordered FeAs layers are shown in Fig. 4. Except for the columnar magnetic order [(iv)] that yields a significant OT split for the TT axes, all other patterns [(i)–(iii)] resulted in an energy minimum for an undistorted TT structure. The inclusion of spin-orbit coupling did not change this result within the numerical error bars. In surprisingly good agreement with our neutron experiments, we obtain a shortening of the $b$ axis along the ferromagnetic columns compared to the $a$ axis along the antiferromagnetic propagation, resulting in a $b/a$ ratio of 0.984 for $SrFe_2As_2$ and

0.987 for the Ba system. These values are only slightly larger than the experimentally observed distortions extrapolated to zero temperature and in excellent agreement with respect to the relative changes between both compounds. Thus, obtaining an OT axes split for the columnar magnetic order only, together with its lowest energy, indicates that this magnetic order and the OT lattice distortion in both compounds are intrinsically tied to each other.

In summary, we report a detailed study of the structural distortion and of the magnetic ordering using x-ray diffraction and $\mu$SR experiments, as well as preliminary neutron-scattering and Mössbauer spectroscopy data. We confirm the low-temperature phase to be analogous to that reported for $BaFe_2As_2$ with an OT structural distortion, space group *Fmmm*, and a columnar antiferromagnetic ordering of the Fe moment with a propagation vector (1,0,1). However, both the structural distortion and the size of the ordered Fe moment are larger in the Sr compound than in the Ba compound. The magnetic and the structural order parameters do not only show a sharp first-order transition at $T_0$ as previously suggested, but evidence the same $T$ dependence in the whole $T$ range from $T_0$ down to lowest temperatures. At $T_0$ both the OT distortion $\delta$ and the muon precession frequency $f_1$ jump to only $\approx$68% of their low-$T$ saturation value. A comparison with x-ray data obtained on single crystals with a lower $T_0$ and a broader transition indicates that the further increase in $\delta(T)$ and $f_1(T)$ below $T_0$ is an intrinsic behavior and not due to defects. The identical $T$ dependence of $\delta(T)$ and $f_1(T)$ proves that the structural and the magnetic order parameters are intimately coupled. In this respect, our data unambiguously indicate that $SrFe_2As_2$ behaves very differently from the picture presently proposed for the RFeAsO compounds, where the SDW is suggested to form in a second-order transition at $\approx$10 K below the structural transition, the two order parameters being disconnected. The strong connection between the magnetic and the structural parameter is not only present in $SrFe_2As_2$, but seems to be a more general property of the $AFe_2As_2$ systems. This is evidenced by a comparison of the magnitude of both order parameters between $SrFe_2As_2$ and $BaFe_2As_2$. From the data of Rotter *et al.*[6] one can deduce $\delta_0=0.36\times10^{-2}$ for $BaFe_2As_2$, which is 37% smaller than $\delta_0=0.56\times10^{-2}$ in $SrFe_2As_2$. The value of the hyperfine field determined in Fe Mössbauer experiments and, thus, the size of the ordered Fe moment also decreases by 36% from $B_{\mathrm{eff}}=8.5$ T in $SrFe_2As_2$ to $B_{\mathrm{eff}}=5.4$ T in $BaFe_2As_2$.[6] Thus, both the magnetic and the structural order parameters scale by about the same amount when going from $SrFe_2As_2$ to $BaFe_2As_2$. Fully relativistic band-structure calculations obtain an OT lattice distortion for the columnar magnetic order only, in very good agreement with the experimental data. This yields strong support to the idea that lattice distortion and the columnar magnetic order in these compounds are intrinsically tied to each other. While finalizing our paper, a study of the structural distortion in $SrFe_2As_2$ and $EuFe_2As_2$ appeared as a preprint, showing similar structural data but suggesting a second-order-type transition.[23]

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