Commensurate Spin Density Wave in LaFeAsO: A Local Probe Study

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We present a detailed study on the magnetic order in the undoped mother compound LaFeAsO of the recently discovered Fe-based superconductor $LaFeAsO_{1-x}F_x$. In particular, we present local probe measurements of the magnetic properties of LaFeAsO by means of ^{57}Fe Mössbauer spectroscopy and muon-spin relaxation in zero external field along with magnetization and resistivity studies. These experiments prove a commensurate static magnetic order with a strongly reduced ordered moment of $0.25(5)\mu_B$ at the iron site below $T_N = 138$ K, well separated from a structural phase transition at $T_S = 156$ K. The temperature dependence of the sublattice magnetization is determined and compared to theory. Using a four-band spin density wave model both, the size of the order parameter and the quick saturation below T_N are reproduced.

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The recently discovered Fe-based superconductors $LaFeAsO_{1-x}F_x$ [1] and the related materials in which La is substituted by Sm, Ce, Nd, Pr, and Gd, respectively, [2–7] has triggered an intense research in the oxypnictides. Besides the high critical temperature above 50 K, there are further striking similarities to the properties of the high-T_C cuprates. The oxypnictides have a layered crystal structure with alternating FeAs and LaO sheets, where the Fe atoms are arranged on a simple square lattice [1]. Theoretical studies reveal a two-dimensional electronic structure [8] and it is believed that conductivity takes place mainly in the FeAs layers while the LaO layers provide the charge reservoir when doped with F ions. Again, similar as in the cuprates, superconductivity emerges when doping a magnetic mother compound with electrons or holes and thereby supressing the magnetic order [9]. This suggests an interesting interplay between magnetism and superconductivity and, indeed, a recent theoretical work suggests that magnetic fluctuations associated with quantum critical point are essential for superconductivity in the electron doped $LaFeAsO_{1-x}F_x$ superconductors [10].

However, in contrast to the cuprates, the magnetic mother compound is not a Mott-Hubbard insulator but a poor metal. A large covalency in the FeAs layers was found [8,11], which in the case of tetragonal LaFePO, i.e., the compound where As is replaced by P, leads to a nonmagnetic ground state [12,13]. In contrast, in LaFeAsO there is an additional structural distortion at elevated temperatures [14,15] and a long range spin density wave (SDW) antiferromagnetic order has been observed in neutron scattering experiments on powder samples below ~150 K [15]. First principle calculations yield antiferromagnetic order with Fe magnetic moments ranging from 1.5 to $2.3\mu_B$ [10,16–18], while the neutron scattering experiments indicate a much smaller value. Assuming that the full sample volume is contributing to the magnetic scattering an ordered moment of $\sim 0.35\mu_B$ [15] is inferred from the weak superlattice reflections in powder neutron diffraction. A local probe measurement, which could verify the type of order and the size of the ordered moment in LaFeAsO, is up to now lacking. It is, however, apparent that a detailed knowledge and understanding of the magnetic properties of LaFeAsO form the basis to tackle the intriguing question about the interplay between magnetism and superconductivity in this new class of superconductors.

In this Letter we report local probe measurements of the magnetic properties of LaFeAsO by means of ^{57}Fe Mössbauer spectroscopy and muon-spin relaxation, both in zero external field. These studies prove a static magnetic order below $T_N = 138$ K with a clearly commensurate spin structure and a strongly reduced ordered moment at the Fe site in the ordered phase. The data provide a high precision measurement of the temperature dependence of the sublattice magnetization which is in fair agreement with a theoretical model assuming a four-band SDW model. The theoretical calculations reproduce the size of the order parameter as well as the quick saturation below T_N, which markedly differs from the conventional mean-field behavior.

Polycrystalline LaFeAsO has been prepared by using a two-step solid state reaction method, similar to that described by Zhu *et al.* [19], and annealed in vacuum. The

crystal structure and the composition were investigated by powder x-ray diffraction and wavelength-dispersive x-ray spectroscopy (WDX). From the x-ray diffraction data impurity concentrations smaller than 1% are inferred. In order to investigate the magnetic order we have performed zero field μSR between 1.6 and 300 K. ^{57}Fe Mössbauer spectroscopy experiments have been done in the temperature range 13 to 180 K [source: ^{57}Co-in-Rh matrix at room temperature; emission line half width at half maximum: 0.130(2) mm/s]. The results of these local probe experiments are compared with magnetization and resistivity data.

Typical Mössbauer spectra are shown in Fig. 1. Above 140 K, the spectra can be fitted with a single Lorentzian line with an isomer shift of $S = 0.52(1)$ mm/s representing LaFeAsO. This is in the typical range of low or intermediate spin Fe(II). Below 140 K, a splitting of the absorption line reveals the formation of a magnetic hyperfine field. In this temperature range the spectra have been analyzed by diagonalizing the hyperfine Hamiltonian including electric quadrupole and magnetic hyperfine interaction. The main result is the observation of a magnetic hyperfine field with a mean saturation value at low temperatures of $B_{hf}(0) = 4.86(5)$ T. The data are consistent with a commensurate antiferromagnetic order of the iron spins. An incommensurate spin density wave can be ruled out since this would lead to a very broad hyperfine field distribution ranging from zero to a maximum field value. In our experiment the hyperfine field distribution is broadenend only slightly indicating a slightly inhomogeneous magnetic state in our sample, which could be caused by small variations of the oxygen content. In order to properly describe the spectra we have used two sextets of equal strength which technically account for the broadening. Both sextets show an electric quadrupole splitting of QS $\approx$ 0.3 mm/s due to a small deformation of the $FeAs_4$ tetrahedron below the structural phase transition [15].

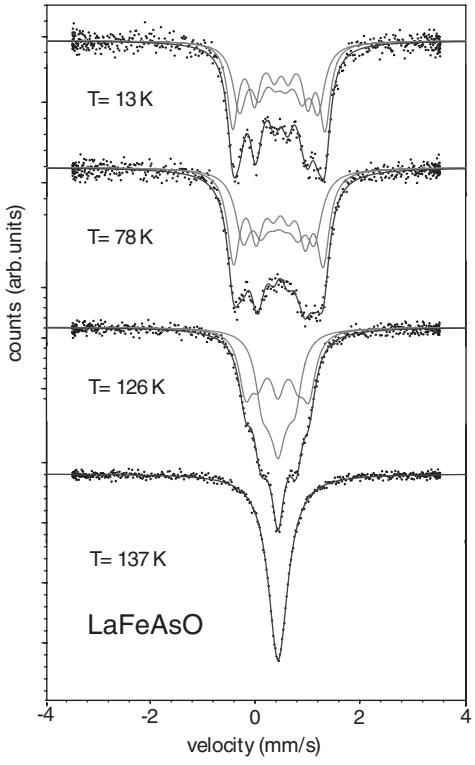

FIG. 1. Typical Mössbauer spectra of a LaFeAsO powder sample. The full lines describe the fit and the subspectra used in the data analysis (see text).

The second important information from the Mössbauer experiments concerns the size of the ordered moment. The hyperfine field of 4.86 T is about 1 order of magnitude smaller than the observed hyperfine field for iron oxide compounds which exhibit a fully ordered moment of $2\mu_B$ [20]. This strongly contradicts all models for the magnetism in LaFeAsO based on local high spin Fe moments. The ordered moment at the Fe site in LaFeAsO can be estimated to $0.25(5)\mu_B$. The error bar in this determination mainly reflects the not well known influence of covalency, i.e., a possible delocalization of spin density from the Fe $3d$ to adjacent As atoms. It is well established that a strong covalency could, in principle, reduce the measured hyperfine field at the iron nucleus as determined by Mössbauer spectroscopy. However, electronic structure calculations reveal only a very small contribution from As orbitals to the electronic bands close to the Fermi level [21] suggesting that the influence of covalency on $B_{hf}(0)$ is weak for LaFeAsO.

Further insight into the magnetic order is obtained from our μSR data. Representative spectra of LaFeAsO for temperatures above and below T_N are shown in Fig. 2. For temperatures above $T_N = 138$ K a weak Gaussian-Kubo-Toyabe [22] like decay of the muon-spin polarization is observed with a relaxation rate of only 0.095(1) MHz which is typical for static and randomly oriented magnetic fields originating from nuclear moments. This relaxation is also found in superconducting $LaFeAsO_{1-x}F_x$ with $x = 0.10$ and 0.075 [9]. Below T_N a spontaneous muon-spin precession with a well-defined frequency is observed which implies a well-defined magnetic field at the muon site. This observation strongly supports our conclusion from the Mössbauer spectroscopy: i.e., an incommensurate spin density wave as well as a spin-glass like order can be excluded.

Analyzing the μSR data in detail proves that 100% of the sample volume magnetically orders at T_N. A proper description of the spectra requires at least a two-component relaxation function indicating magnetically different muon sites. For temperatures above $\sim$70 K a well-defined frequency is observed for about 70% of the muons while about 30% show a strong relaxation due to a broad static field distribution. This situation changes below 70 K where a third component with a low frequency precession ($\approx$3 Mhz) appears which is clearly visible in the raw data at 1.6 K (see Fig. 2). As can be seen from the temperature dependence of the signal fractions shown in

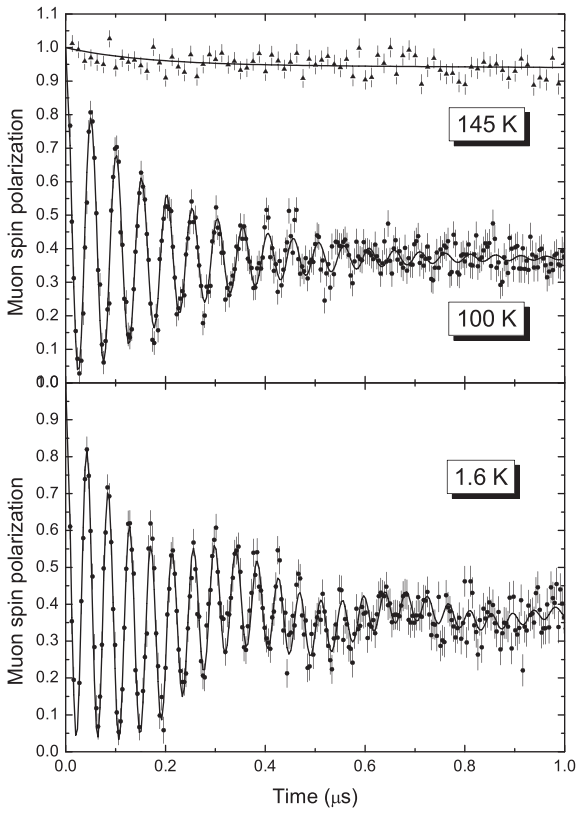

FIG. 2. Zero field μSR spectra of LaFeAsO for 1.6, 100, and 145 K.

Fig. 3, this signal develops on the cost of the strongly damped fraction.

The high precession frequency of the first signal implies that these muons reside very close to the Fe magnetic moments in the FeAs layers. We associate the weaker signals with more remote muon sites, most likely near the LaO layers. All muon sites show the development of magnetic order below $T_N = 138$ K. At present we have no explanation for the change of the weaker signal below 70 K but emphasize that it is intrinsic to LaFeAsO.

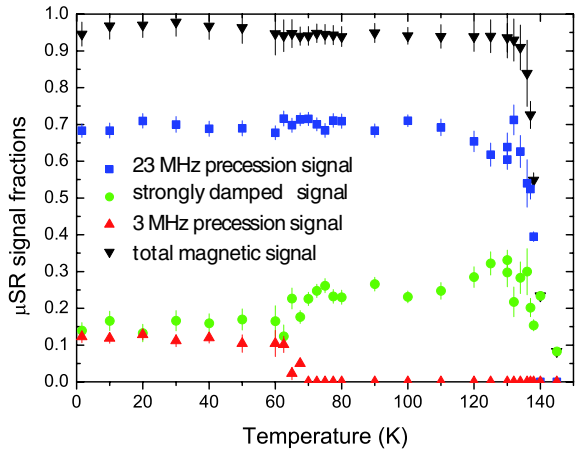

FIG. 3 (color online). Temperature dependence of the μSR signal fractions (see text).

In the literature, evidence for spin density order has been extracted from magnetization and transport data. Corresponding measurements for our sample are displayed in Fig. 4. Both, the electrical resistivity and the magnetization show a clear anomaly at $T_s \approx 156$ K, i.e., well above the magnetic ordering temperature T_N. Subsequent temperature dependent XRD studies [23] prove that at this temperature the tetragonal to orthorhombic structural phase transition occurs which has been observed in recent diffraction measurements [14,15]. Anomalies of ρ and χ are also found at T_N when the temperature derivatives are considered, as shown in Fig. 4. Both derivatives exhibit a peak-like anomaly at exactly the same temperature where the magnetic transition occurs according to our local probe studies.

Recently, the phase transition at T_S has been discussed in connection with the formation of an "electron nematic phase" and broken Ising symmetry [24,25]. The pronounced anomalies of ρ and χ clearly demonstrate an intimate coupling between the structural phase transition on the one hand and the electronic and magnetic properties on the other hand. At T_S the conductivity starts to increase and, surprisingly, this increase becomes weaker at T_N; i.e., magnetic ordering does not cause a decrease of electron scattering. The decrease of χ at T_S shows an enhancement of antiferromagnetic correlations at the structural phase transition. The anomaly of χ at T_N is qualitatively very similar, but much weaker. Indeed, analyzing the magnetic specific heat, which is proportional to $\partial(\chi T)/\partial T$, yields a much smaller jump at T_N than at T_S. This strong impact of the structural transition on the magnetism is, however, not visible in our local probe experiments. At 140 K the μSR data show only a small volume fraction of $\approx$20% with static local fields, above 145 K we can rule out any static local magnetic fields. This is typical for a small distribution

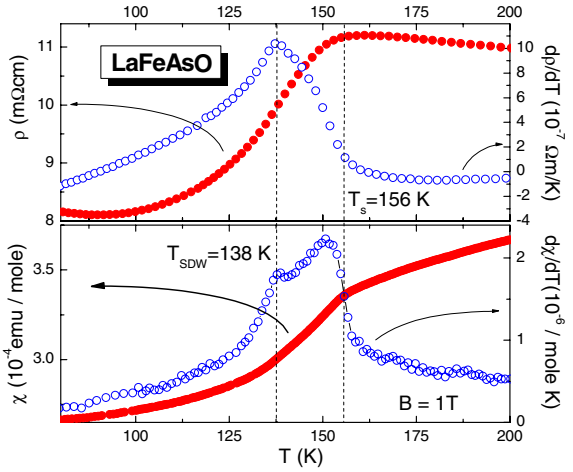

FIG. 4 (color online). Temperature dependence of (top) the electrical resistivity and (bottom) the magnetization vs temperature and the respective derivatives $\partial\chi/\partial T$ and $\partial\rho/\partial T$. T_S and T_N mark the structural phase transition at 156 K and the SDW-formation at 138 K.

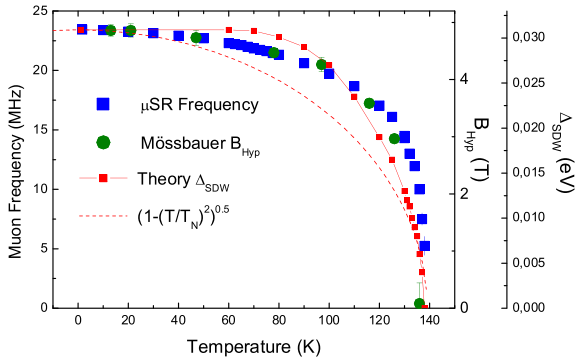

FIG. 5 (color online). Temperature dependence of the main zero field μSR frequency, the Mössbauer hyperfine field and the calculated SDW order parameter.

of ordering temperatures within the powder sample. Moreover, there are no signatures of slow spin fluctuations on the time scale of the Mössbauer and the μSR experiment above this temperature.

In order to compare our results with theoretical models we analyze the temperature dependence of the the magnetic order parameter obtained from the main muon-spin precession frequency and the static magnetic hyperfine field B_{hf} measured by Mössbauer spectroscopy. As displayed in Fig. 5 both quantities exhibit the same behavior.

In the following we analyze the experimental data within a conventional SDW picture. As has been shown previously [26], the effective low-energy band structure of the undoped LaFeAsO can be modeled by a single-electron model Hamiltonian. For the four-band model considered here the effective interaction will consist of an on-site Hubbard intraband repulsion U and the Hund's coupling J. There is also an interband Hubbard repulsion U', which however does not contribute to the RPA susceptibility. As shown by two of us earlier [26] the main magnetic instability in the folded Brillouin Zone occurs at the antiferromagnetic wave vector $\mathbf{Q}_{\mathrm{AFM}} = (\pi, \pi)$ due to the interband nesting between the hole α- and the electron β-bands [16,21,26–28]. Setting the Hund coupling to $J = 70$ meV and choosing $U = 320$ meV we obtain the ordering temperature $T_N = 138$ K using multiband RPA susceptibility.

Below T_N the condition for the SDW instability can be regarded as a mean-field equation for the SDW order parameter, Δ_{SDW}. Solving this equation self-consistently we obtain the temperature dependence of $\Delta_{\mathrm{SDW}}(T)$ as shown in Fig. 5. Because of the multiorbital character of the equation we find that the SDW gap reaches its saturation rather quickly below T_N and the resulting temperature dependence deviates from the usual $\sqrt{1-(T/T_N)^2}$ temperature dependence. In the experiment a slightly stronger initial increase below T_N and further small differences between experiment and theory at lower temperatures are observed. This may be due to the importance of the thermal fluctuations neglected here and/or fine details of the band structure.

From the value $\Delta_{\mathrm{SDW}}(T = 0\ \mathrm{K}) = 31$ meV we can also estimate the magnetic moment per Fe site to be $\mu \approx 0.33\mu_B$. Considering that this mean-field model does not fully include quantum fluctuations a value larger than the experimentally observed one is expected.

In conclusion, we present a detailed study of the magnetic order in LaFeAsO by means of the local probe techniques Mössbauer spectroscopy and μSR along with magnetization and resistivity studies. These experiments prove a commensurate static magnetic order with a strongly reduced ordered moment of $0.25(5)\mu_B$ at the iron site below $T_N = 138$ K, well separated from a structural phase transition at $T_S = 156$ K. A calculation using a four-band SDW model reproduces the size of the order parameter and the quick saturation below T_N.

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[1] Y. Kamihara *et al.*, J. Am. Chem. Soc. **130**, 3296 (2008).
[2] X. H. Chen *et al.*, arXiv:0803.3603.
[3] G. F. Chen *et al.*, Phys. Rev. Lett. **100**, 247002 (2008).
[4] Z.-A. Ren *et al.*, Europhys. Lett. **82**, 57 002 (2008).
[5] Z.-A. Ren *et al.*, arXiv:0803.4283.
[6] P. Cheng *et al.*, Science in China (Series G) **51**, 719 (2008).
[7] Z.-A. Ren *et al.*, Chin. Phys. Lett. **25**, 2215 (2008).
[8] D. J. Singh and M. H. Du, Phys. Rev. Lett. **100**, 237003 (2008).
[9] H. Luetkens *et al.*, arXiv:0804.3115 [Phys. Rev. Lett. (to be published)].
[10] G. Giovannetti *et al.*, arXiv:0804.0866.
[11] K. Haule *et al.*, Phys. Rev. Lett. **100**, 226402 (2008).
[12] S. Lebègue, Phys. Rev. B **75**, 035110 (2007).
[13] C. Y. Liang *et al.*, Supercond. Sci. Technol. **20**, 687 (2007).
[14] T. Nomura *et al.*, arXiv:0804.3569.
[15] C. Cruz *et al.*, Nature (London) **453**, 899 (2008).
[16] J. Dong *et al.*, Europhys. Lett. **83**, 27006 (2008).
[17] F. Ma *et al.*, arXiv:0803.3286 [Phys. Rev. B (to be published)].
[18] C. Cao *et al.*, Phys. Rev. B **77**, 220506 (2008).
[19] X. Zhu *et al.*, Supercond. Sci. Technol. **21**, 105001 (2008).
[20] N. N. Greenwood and T. C. Gibb, Mössbauer Spectroscopy, London 1971.
[21] I. Mazin *et al.*, arXiv:0803.2740 [Phys. Rev. Lett. (to be published)].
[22] R. S. Hayano *et al.*, Phys. Rev. B **20**, 850 (1979).
[23] H. Luetkens *et al.*, (to be published).
[24] C. Xu, M. Müller, and S. Sachdev, Phys. Rev. B **78**, 020501 (2008).
[25] C. Fang *et al.*, Phys. Rev. B **77**, 224509 (2008).
[26] M. Korshunov and I. Eremin, arXiv:0804.1793.
[27] H.-J. Zhang *et al.*, arXiv:0803.4487.
[28] S. Raghu *et al.*, Phys. Rev. B **77**, 220503 (2008).