

A ^{57}Fe Mössbauer Spectroscopy Study of the 7 K Superconductor LaFePO

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A polycrystalline sample of superconducting LaFePO was prepared in a tin flux at 1123 K. The structure was determined from single-crystal data (ZrCuSiAs type, $P4/nmm$, $a = 3.9610(1)$, $c = 8.5158(2)$ Å, $Z = 2$), and the phase analysis was performed by the Rietveld method. LaFePO is Pauli-paramagnetic and becomes superconducting at 7 K after removing the ferromagnetic impurity phase Fe₂P from the sample. ^{57}Fe Mössbauer spectroscopy measurements at 298, 77, 4.2, and 4 K show single signals at isomer shifts around 0.35 mm s^{-1} , subject to weak quadrupole splitting. At 4 K, a symmetric line broadening appears, resulting from a small transferred magnetic hyperfine field of $1.15(1)$ T and accompanied by an angle of $54.7(5)^\circ$ between B_{hf} and V_{zz} , the main component of the electric field gradient tensor.

Key words: Pnictide Oxide, Iron, Superconductivity, Mössbauer Spectroscopy

Introduction

The recent discovery of high- T_{C} superconductivity in the fluoride-doped quaternary iron arsenide oxides $\text{REFeAs}(\text{O}_{1-x}\text{F}_x)$ ($\text{RE} = \text{La}–\text{Sm}$) [1] with critical temperatures (T_{C}) up to 55 K [2] has sparked a tremendous interest in compounds with the ZrCuSiAs-type structure [3]. The parent compound LaFeAsO does not become superconducting, but shows a spin density wave (SDW) anomaly at 150 K and antiferromagnetic ordering below 138 K [4, 5]. When doping the oxide site with fluoride, the SDW is suppressed, and superconductivity occurs at critical temperatures up to 41 K in the iron arsenide oxide LaFeAs(O_{1-x}F_x) [6]. On the other hand, the iron phosphide oxide LaFePO had previously been reported to become superconducting at 3.5–4.1 K even in the undoped form [7, 8]. Upon fluoride doping, the T_{C} had been reported to increase slightly to 6 K. Such large differences in T_{C} between the phosphide and arsenide oxides do not occur in the isotopic nickel compounds LaNiPO [9, 10] and LaNiAsO [11]. Both compounds are superconductors around 2–4 K, and up to now, their low transition temperatures could not be increased significantly by doping.

These results emphasize the exceptional position of the iron arsenide oxides. One key factor for their higher

T_{C} obviously is the existence of a SDW in the undoped phase, which becomes unstable around 150 K, before it locks into an antiferromagnetic spin ordering. This suggests that spin fluctuations play an important role in the pairing mechanism, similar as in the high- T_{C} cuprates. It is not known up to now if a comparable magnetic anomaly also occurs in superconducting LaFePO. However, the much lower T_{C} and its insignificant increase upon doping could imply that the pairing mechanism is different in phosphide and arsenide oxides.

Recent investigations on the magnetic properties of doped and undoped LaFeAsO by ^{57}Fe Mössbauer spectroscopy have proved spin ordering in LaFeAsO and its suppression upon doping [12, 13]. In order to shed light on a potentially different nature of superconductivity in the corresponding phosphide oxide, we present ^{57}Fe Mössbauer spectra, magnetic measurements and structural details of LaFePO in this paper.

Experimental Section

Synthesis

A polycrystalline sample of LaFePO was synthesized by heating a mixture of La, Fe, Fe₂O₃, and red P in a ratio of 3 : 1 : 1 : 3 (a total of ~ 650 mg) in a tin flux (2.5 g tin) [14] under argon atmosphere by using an alumina crucible in a

Formula	LaFePO	<i>hkl</i> range	$\pm 5, \pm 5, \pm 11$
M_r	241.726	$(\sin \theta / \lambda)_{\max}, \text{\AA}^{-1}$	1.152
Cryst. size, mm^3	$0.043 \times 0.05 \times 0.015$	Refl. measured	1976
Crystal system	tetragonal	Refl. unique	102
Space group	$P4/nmm$	R_{int}	0.107
$a, \text{\AA}$	3.9610(1)	Param. refined	11
$c, \text{\AA}$	8.5158(2)	$R(F)/wR(F^2)$ (all)	0.043, 0.105
$V, \text{\AA}^3$	133.61(1)	GoF (F^2)	1.173
Z	2	$D_{\text{calcd}}, \text{g cm}^{-3}$	6.07
$\mu(\text{MoK}\alpha), \text{cm}^{-1}$	21.454		
Atomic positions and displacement parameters			
Atom	Wyckoff	z	$U_{\text{eq}} (\text{pm}^2)$
La	2c (1/4, 1/4, z)	0.1496(2)	96(8)
Fe	2b (3/4, 1/4, 1/2)	1/2	91(9)
P	2c (1/4, 1/4, z)	0.6362(6)	93(13)
O	2a (3/4, 1/4, 0)	0	60(30)
Selected bond lengths (\AA) and angles (deg)			
La–O ($4\times$)	2.355(1)	Fe–P ($4\times$)	2.295(3)
La–P ($4\times$)	3.343(3)	Fe–Fe ($4\times$)	2.801(1)
La–O–La	107.0(1), 114.5(1)	P–Fe–P	104.8(1), 119.3(2)

Table 1. Crystal structure data for LaFePO.

silica ampoule. The sample was heated at 1123 K (40 K h^{-1}) for 7 d and slowly cooled to r. t. (15 K h^{-1}). The tin ingot was dissolved in 6 M HCl at r. t. This procedure yielded a black powder consisting of platelet crystals with a metallic lustre.

X-Ray diffraction

X-Ray powder patterns of the LaFePO sample were recorded on a Stoe Stadi-P diffractometer ($\text{MoK}\alpha_1$, Ge(111) monochromator, $\lambda = 70.93 \text{ pm}$, Si as external standard). The powder data were analyzed by the Rietveld method using the GSAS suite [15]. Single-crystal data of LaFePO were collected using an Enraf-Nonius κ -CCD diffractometer equipped with a rotating anode ($\text{MoK}\alpha$ radiation, $\lambda = 71.073 \text{ pm}$). Intensities were corrected for absorption with the program SADABS [16] and refined against F^2 using SHELXL-97 [17] with anisotropic displacement parameters for all atoms except oxygen. Starting parameters were taken from isostructural PrFePO [18]. Details are given in Table 1.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-391428.

Magnetic measurements

Magnetization measurements were performed using a Quantum-Design SQUID magnetometer (MPMS-XL5) between 1.8 and 300 K. A powdered sample of LaFePO was placed into a gelatine capsule and fixed in a straw as sample holder. Zero-field-cooling (Shielding) and field-cooling (Meissner) measurement cycles were performed at 10 Oe between 1.8 and 12 K in the reciprocating sample option (RSO)

mode. The magnetic susceptibility between 2 and 300 K was measured at 10 kOe.

^{57}Fe Mössbauer spectroscopy

A $^{57}\text{Co}/\text{Rh}$ source was available for the ^{57}Fe Mössbauer spectroscopy investigations. The LaFePO sample was placed in a thin-walled PVC container at a thickness of about 10 mg Fe cm^{-2} . The measurements were run in the usual transmission geometry at 298, 77, 4.2, and 4 K. The source was kept at r. t.

Results and Discussion

The ZrCuSiAs -type structure [19] was confirmed by single-crystal data. LaFePO is built up by LaO and FeP layers alternating along [001]. Lanthanum is eight-fold coordinated by four oxygen (2.355 \AA) and four phosphorus atoms (3.343 \AA). The Fe–P bonds lengths (2.295 \AA) are close to the sum of the covalent radii of iron and phosphorus (2.26 \AA , [20]). The FeP_4 tetrahedra are slightly flattened along [001], as can be recognized by a P–Fe–P angle of 119.3° . This distortion is slightly larger than in LaFeAsO with an As–Fe–As angle of 113.7° (at 175 K) [4], but much smaller than that of the NiP_4 tetrahedra in LaNiPO , where the P–Ni–P angle is 126.5° [9].

The Rietveld analysis revealed that the sample was not single phase, small amounts of Fe_2P and FeSn_2 being detected. Such magnetic impurity phases can be very destructive for susceptibility measurements. Fe_2P is ferromagnetic below 266 K [21] and FeSn_2 is antiferromagnetic below 380 K [22], thus even

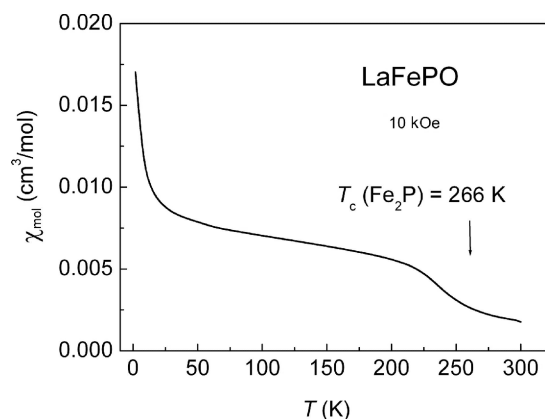


Fig. 1. Magnetic susceptibility of the LaFePO sample measured at 10 kOe.

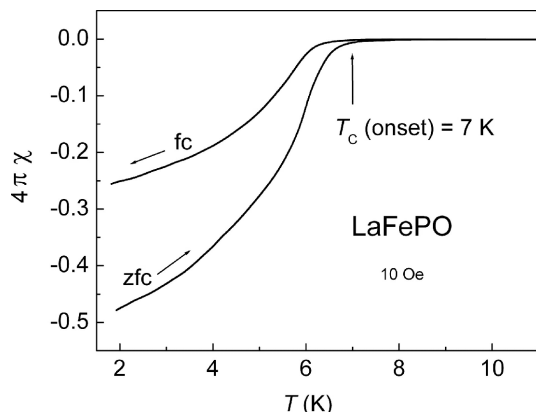


Fig. 2. Diamagnetic shielding (zfc) and Meissner-Effect (fc) of LaFePO.

traces of Fe_2P would strongly affect the magnetic measurements. This is especially important with respect to the weak Pauli-paramagnetic LaFePO. Indeed, our first susceptibility measurement of the LaFePO sample showed a strong upturn of χ below 270 K, which coincides with the Curie point of Fe_2P , and no superconductivity could be detected at temperatures down to 1.8 K. In order to remove impurities, we separated ferromagnetic particles by stirring a suspension of the finely grounded LaFePO sample in liquid N_2 with a strong permanent magnet. After this treatment, the Fe_2P impurity was drastically reduced and we could successfully fit the complete X-ray powder pattern with phase fractions of 96 % LaFePO and 4 % FeSn_2 . The magnetic measurement of this purified sample still revealed small traces of a residual Fe_2P impurity, as depicted in Fig. 1, but now the sample exhibited the typical strong diamagnetic shielding of a superconductor.

Table 2. Fitting parameters for ^{57}Fe Mössbauer spectroscopy data of LaFePO. δ : isomer shift; Γ : experimental line width; ΔE_Q : quadrupole splitting parameter.

T (K)	δ (mm s^{-1})	Γ (mm s^{-1})	ΔE_Q (mm s^{-1})
298	0.24(1)	0.32(3)	0.11(3)
77	0.34(1)	0.28(4)	0.12(3)
4.2	0.36(1)	0.37(3)	0.19(2)
4	0.36(1)	0.32(1)	0.15(1)

The complete shielding and Meissner cycles (Fig. 2) clearly show the onset of superconductivity at 7 K, which is significantly higher than 4.1 K as reported for undoped LaFePO [7, 8]. Obviously, the superconductivity was completely suppressed by the ferromagnetic impurity phase, which generates a magnetic field inside the sample. If the critical field of the superconducting phase is sufficiently small, this additional field can lower T_C or even bring it to zero. Our magnetization measurements at 1.8 K showed small critical fields of $H_{c1} \approx 75$ Oe and $H_{c2} \approx 880$ Oe for LaFePO, which correspond approximately to the values given by Hosono [8].

Our results indicate that ferromagnetic impurities can strongly influence the superconductivity in LaFePO and presumably also in the LaFeAsO compounds. This may be one reason for some different T_C 's of supposedly identical compounds, which are in most cases far from being single phase. However, in the case of fluoride-doped compounds, the exact amount of fluoride in the structure may be another important problem.

^{57}Fe Mössbauer spectra of LaFePO recorded at 298, 77, 4.2, and 4 K are presented in Fig. 3 together with transmission integral fits. The corresponding fitting parameters are listed in Table 2. In agreement with the ZrCuSiAs -type crystal structure, the spectra were well reproduced with single iron sites at isomer shifts around 0.3 mm s^{-1} , slightly smaller than the isomer shifts observed recently for LaFeAsO and $\text{LaFeAsO}_{0.89}\text{F}_{0.11}$ [12, 13]. Due to the non-cubic site symmetry, the spectra are subject to weak quadrupole splitting.

Similar to LaFeAsO and $\text{LaFeAsO}_{0.89}\text{F}_{0.11}$, we observe a slight increase of the isomer shift also for LaFePO with decreasing temperature. For iron, a smaller isomer shift is consistent with a higher electron density at the nuclei [23]. The isomer shifts observed for LaFePO are comparable with those of other iron phosphides with tetrahedrally coordinated iron [24, 25].

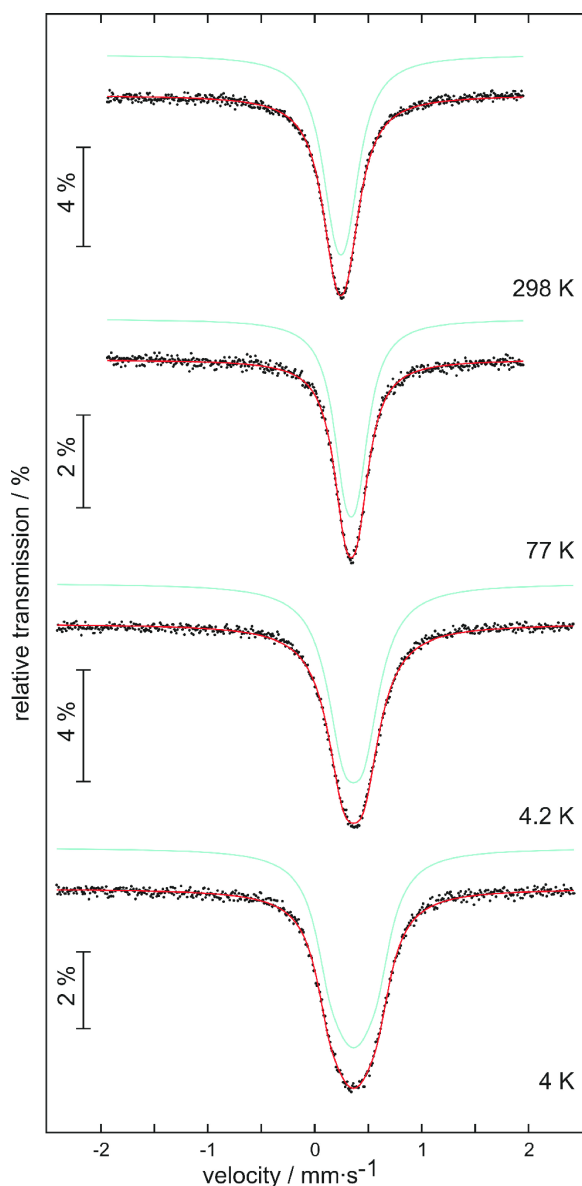


Fig. 3. Experimental and simulated ^{57}Fe Mössbauer spectra of LaFePO at 298, 77, 4.2, and 4 K.

At 298 and 77 K, we observe no magnetic hyperfine field splitting, clearly manifesting the absence of mag-

netic ordering, similar to the fluoride doped superconducting arsenide $\text{LaFeAsO}_{0.89}\text{F}_{0.11}$ [12, 13]. Since a strong anomaly has been observed in the specific resistivity of LaFeAsO [5], associated with a spin-density wave, and full magnetic hyperfine field splitting below this phase transition is evident from ^{57}Fe Mössbauer spectroscopy, we suppose that the mechanism for superconductivity in LaFeAsO and LaFePO is different. This is also supported by the facts that the parent compound LaFeAsO is not superconducting while LaFePO is, and that LaFeAsO becomes superconducting at high T_C upon doping, whereas T_C increases only insignificantly for doped LaFePO . Different mechanisms of superconductivity for iron and nickel pnictide oxides have also been suggested by theoretical arguments [26].

The 4 K spectrum shows a symmetric line broadening. A reliable fit was obtained by simultaneously applying a weak quadrupole splitting of $0.15(1) \text{ mm s}^{-1}$ and a transferred magnetic hyperfine field (B_{hf}) of $1.15(1) \text{ T}$. In order to explain the symmetric spectrum with a combined hyperfine field and an electrical quadrupole interaction, the angle θ between B_{hf} and V_{zz} (the main component of the electric field gradient tensor) should be close to the magic angle. Indeed, the refined θ value for LaFePO was $54.7(5)^\circ$. This behavior has also been observed for other magnetically ordered rare earth phases [27, 28].

This behavior was already evident from a detail of the 4.2 K spectrum, however, the very small transferred hyperfine field is hidden in the slightly increased line width and quadrupole splitting parameters, hampering independent refinement of the hyperfine field parameter. Although our experimental setup is limited to 4 K, we expect higher transferred hyperfine fields at lower temperatures.

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