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2008 J. Phys.: Condens. Matter 20 292201

(http://iopscience.iop.org/0953-8984/20/29/292201)

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IOP Publishing
Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter **20** (2008) 292201 (4pp)
doi:10.1088/0953-8984/20/29/292201

FAST TRACK COMMUNICATION

^{57}Fe Mössbauer spectroscopy and magnetic measurement studies of oxygen deficient LaFeAsO

Israel Nowik[1], Israel Felner[1], V P S Awana[2,3,4], Arpita Vajpayee[2] and H Kishan[2]

[1] Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel
[2] National Physical Laboratory, New Delhi-110012, India

E-mail: awana@mail.nplindia. ernet.in

Received 27 May 2008, in final form 9 June 2008
Published 26 June 2008
Online at stacks.iop.org/JPhysCM/20/292201

Abstract

We report on the magnetic behavior of the oxygen deficient $LaFeAsO_{1-x}$ ($x \sim 0.10$) compound, prepared by one-step synthesis, which crystallizes in the tetragonal (SG $P4/nmm$) structure at room temperature. Resistivity measurements show a strong anomaly near 150 K, which is ascribed to the spin density wave instability. On the other hand, dc magnetization data show paramagnetic-like features down to 5 K, with an effective moment of 0.83 μ_B/Fe. ^{57}Fe Mössbauer studies (MS) have been performed at 95 and 200 K. The spectra at both temperatures are composed of two sub-spectra. At 200 K the major one (88%) is almost a singlet, and corresponds to those Fe nuclei which have two oxygen ions in their close vicinity. The minor one, with a large quadrupole splitting, corresponds to Fe nuclei which have vacancies in their immediate neighborhood. The spectrum at 95 K exhibits a broadened magnetic split major (84%) sub-spectrum and a very small magnetic splitting in the minor sub-spectrum. The relative intensities of the sub-spectra lead to estimating the actual amount of oxygen vacancies in the compound to be 7.0(5)%, instead of the nominal $LaFeAsO_{0.90}$. These results, when compared with reported ^{57}Fe MS of non-superconducting LaFeAsO and superconducting $LaFeAsO_{0.9}F_{0.1}$, confirm that the $LaFeAsO_{0.93}$ studied is a superconductivity–magnetism crossover compound of the newly discovered Fe based superconducting family.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recent reports on superconductivity (SC) up to 54 K in ReFeAsO (Re = La, Pr, Sm, Nd, Gd) have renewed the interest of the scientific community in the research into high T_c superconductors outside of the cuprate family [1–5]. Further, this discovery led the theoreticians to consider high T_c systems outside of the cuprates [6–8]. In the ReFeAsO system, SC is confined to the Fe–As layers and the charge carriers are provided from the doping of fluorine or alternatively by depletion of oxygen from the RE–O planes [1]. This is similar to the high T_c cuprate superconductors case, where SC resides in Cu–O_2 planes and carriers are provided from other nearby layers. One of the most striking properties of the new Fe based superconductors is their seemingly very high upper critical field (H_{c2}) [9, 10]. In contrast to the cuprates, the SC Fe based compounds are prepared and studied by a limited number of research groups. This is due to the complicated synthesis route [1–5, 9, 10], which requires high pressure, high temperature facilities (HPHT, 6 GPa, 1350 °C) [2, 3] and two-step normal pressure synthesis [1, 4]. In fact the

[3] Address for correspondence: National Physical Laboratory, Dr K S Krishnan marg, New Delhi-110012, India.
[4] www.freewebs.com/vpsawana/

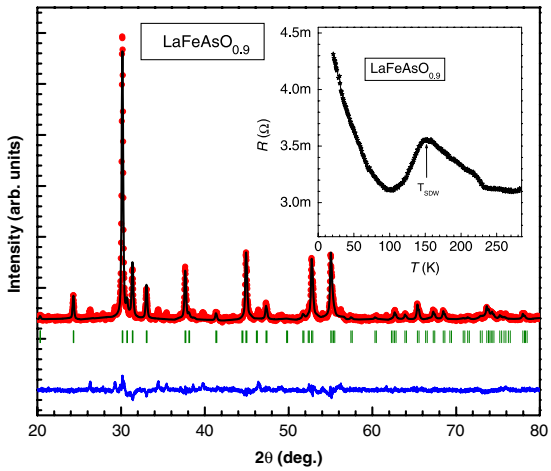

Figure 1. Fitted and observed x-ray diffraction patterns of nominal $LaFeAsO_{0.9}$, and its R–T plot (inset).

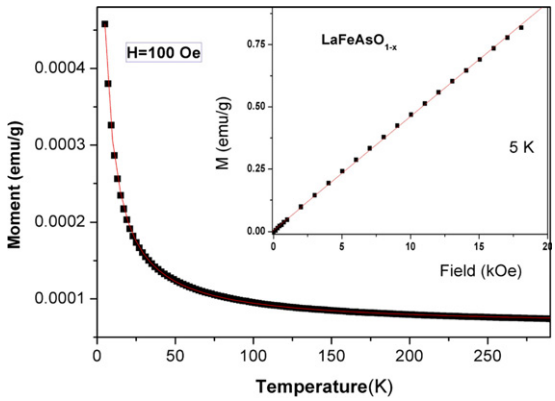

Figure 2. The temperature dependence of the magnetization for $LaFeAsO_{1-x}$ and the isothermal $M(H)$ measured at 5 K (inset).

materials still require optimization in their phase purity, and the appearance of SC depends strongly on the F (fluorine) content or alternatively on the oxygen deficiency. An Indian group have managed to synthesize the nominal non-SC $LaFeAsO_{0.90}$ compound via a relatively simple one-step route [11]. Here, we report on magnetization and ^{57}Fe MS studies of this compound. The interpretation of the MS adopted the method used in our recent publication on SC oxygen deficient $SmFeAsO_{0.85}$ sample, in which coexistence of SC and magnetic order in the Fe–As layers has been observed [10]. The Fe ions are very sensitive to their local environment, and exhibit two sub-spectra; their intensity defines the oxygen vacancy concentration (value of x).

2. Experimental details

Stoichiometric amounts of better than 3N purity of As, Fe, La metal and La_2O_3 were weighed and mixed thoroughly in the nominal composition of $LaFeAsO_{0.9}$ (Fe + As + $0.3La_2O_3$ + 0.4La). A pellet powder, sealed in evacuated quartz tubes (better than 10^{-4} Torr), was heated at 500, 850 and 1100 °C for 12, 12 and 33 h respectively in a single-step procedure [11]. The room temperature x-ray diffraction (XRD) pattern was taken using a Rigaku mini-flex diffractometer. The resistivity measurements, in the temperature range of 12–300 K, were carried out by a four-probe method in a closed cycle refrigerator. Zero-field cooled and field cooled dc magnetic measurements in the range of 5–300 K were performed in a commercial (Quantum Design) superconducting quantum interference device (SQUID) magnetometer. Mössbauer spectroscopy studies were performed by using a conventional constant acceleration drive and a 50 mCi ^{57}Co:Rh source. The velocity calibration was done at RT with an α-Fe absorber and the isomer shift (IS) values are relative to that of iron. The observed spectra were least square fitted with theoretical spectra, assuming a distribution of hyperfine interaction parameters, corresponding to inequivalent iron locations differing in local environment.

3. Results and discussion

Figure 1 depicts the fitted and observed XRD patterns of the $LaFeAsO_{1-x}$ compound studied and its resistance versus temperature (R–T) is shown in the inset. The compound crystallizes in tetragonal structure (space group $P4/nmm$) with lattice parameters $a = 4.0339(2)$ Å and $c = 8.7346(7)$ Å. The fitting parameters, and the site positions of the various atoms, are given in [11]. The R–T plot (figure 1, inset) of $LaFeAsO_{1-x}$ shows typical metallic behavior below 150 K and a semiconductor-like resistivity upturn below 100 K. The metallic step at 150 K is related to the spin density wave (SDW) ordered state of this compound [11]. Neutron diffraction (ND) studies indicate that below 150 K, the tetragonal structure becomes monoclinic and belongs to space group $P112/n$ [12].

The temperature dependence of the magnetization for $LaFeAsO_{1-x}$ measured at 100 Oe is shown in figure 2. The SDW features are not visible and the curve obtained has the typical paramagnetic (PM) shape and adheres closely to the Curie–Weiss (CW) law: $\chi(T) = \chi_0 + C/(T - \theta)$, where χ_0 is the temperature independent part of χ, C is the Curie constant, and θ is the CW temperature. The parameters obtained are: $\chi_0 = 6.5 \times 10^{-6}$ emu g^{-1} Oe^{-1}, $C = 3.07 \times 10^{-4}$ emu T g^{-1} Oe^{-1} which yields a PM effective moment of $P_{\text{eff}} = 0.83\ \mu_B$, and $\theta = -2.8$ K. Presumably, this effective moment corresponds to divalent Fe ions since all other ions are non-magnetic. This P_{eff} is consistent with the low ordered moment ($\sim$0.25 μ_B) at the Fe site in LaFeAsO deduced from ND, μSR and Mössbauer studies [12, 13].

Note that no magnetic susceptibility data have been published yet on the magnetic (SDW) ReFeAsO material. It is impossible to see from dc susceptibility studies an anomaly in the SDW transition. Let us assume an AFM commensurate structure with moments of 0.2–0.3 μ_B, which are anti-parallel to each other. In such a situation the transition is barely visible. For a periodic spin function with such a small moment no anomaly is observed. For example the SDW for Co spins in layered cobalt oxide ($Ca_3Co_4O_9$) is readily observed in spin resonance (μSR) but not in magnetic studies [14].

The MS spectra of $LaFeAsO_{1-x}$ measured below and above the magnetic transition are shown in figure 3, and

Table 1. The hyperfine interaction parameters for $LaFeAsO_{1-x}$ derived from the analysis of the Mössbauer spectra. INT, GAM, IS, EQ and H_{eff} stand for relative intensity, linewidth, isomer shift, quadrupole parameter (EQ $= eqQ/4$) and magnetic hyperfine field.

T (K)	INT(1) (%)	GAM (mm s^{-1})	IS (1) (mm s^{-1})	EQ(1) (mm s^{-1})	H_{eff} (1) (kOe)	INT(2) (%)	GAM (mm s^{-1})	IS(2) (mm s^{-1})	EQ(2) (mm s^{-1})	H_{eff} (2) (kOe)
95	84	0.25(1)	0.57(1)	0	51(2)	16(2)	0.25(1)	0.46(1)	−0.86(1)	8 (1)
200	88	0.30(1)	0.51(1)	0	0	12.0(3)	0.25(1)	0.35(1)	0.89(1)	0

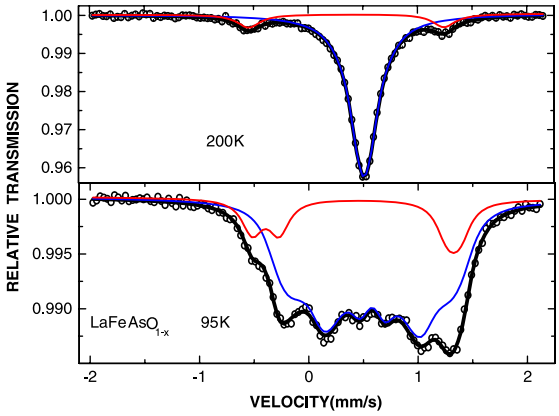

Figure 3. The Mössbauer spectra of $LaFeAsO_{1-x}$ measured at 95 and 200 K.

the deduced hyperfine interaction parameters are listed in table 1. In both tetragonal $P4/nmm$ and monoclinic $P112/n$ structures each Fe, which resides in the 2b or 2f crystallographic positions respectively, has two oxygen ions as nearest neighbors along the crystal c-axis with the shortest Fe–O distance of $c/2 \sim 4.2035$ Å. Each spectrum in figure 3 is composed of two sub-spectra and the isomer shift (IS) values for both sites are typical for a divalent low spin state for all Fe ions. At 200 K the intense sub-spectrum (∼88%) is almost a singlet, and corresponds to those iron nuclei which have two oxygen ions in their close vicinity. The second quadrupole doublet corresponds to iron nuclei which have vacancies in their immediate neighborhood. In the case of a random distribution of vacancies, the probability for an iron ion (in this layered structure) to have one or two vacancies as first-nearest neighbors is $2x(1-x)$ and x^2, respectively. Thus the intensity of the minor site in the 200 K spectrum (12.0(3)%) indicates that for this material $x = 0.065$ (and not 0.10). The probability of having iron with two neighboring vacancies is small and negligible. At 95 K both sites are magnetically ordered and the hyperfine parameters deduced are presented in table 1. The major sub-spectrum was analyzed in terms of a very asymmetric Gaussian distribution of magnetic hyperfine fields (H_{eff}). The field distribution results probably due to a partly incommensurate spin density wave [15] caused by the vacancies. The value of H_{eff} at maximum probability is ∼50 kOe, similar to the low fields observed for the non-SC and magnetic LaFeAsO compound [16]. The minor sub-spectrum (16(2)%) has a large quadrupole splitting, like at 200 K, with a small magnetic splitting; see table 1.

The hyperfine parameters of the major sub-spectrum are identical at the two temperatures and are very similar to values obtained for other SC compounds such as $SmFeAsO_{0.85}$ [10] $LaFeAsO_{0.89}F_{0.11}$ [16] and LaFePO [17]. For these samples the MS exhibit only one singlet, since no vacancies exist and therefore no second sub-spectrum is achieved. The vacancies obtained in our sample induce two types of Fe ions, and thus permit direct insight into the various Fe ion behaviors. Similarly, two sub-spectra were obtained for the oxygen deficient $SmFeAsO_{0.85}$ [10].

In conclusion, we present a detailed study of the magnetic nature of the oxygen deficient $LaFeAsO_{1-x}$ compound, by means of resistivity, dc magnetic measurements and Mössbauer spectroscopy studies. The resistivity curve shows that a peak at 150 K which is related to the SDW instability occurs for this sample. On the other hand, no anomaly is observed in the dc $M(T)$ plot which rather shows a PM-type behavior over the entire temperature range. As mentioned before, the SDW is barely seen in $M(T)$, but is visible in $R(T)$ and MS. The MS as a local probe senses the SDW features. The sample is magnetic at low temperatures. However $M(T)$, as a bulk measurement, cannot be used to detect the wave-like spin density changes in the system. Due to oxygen vacancies, the MS spectra below and above 150 K are composed of two sub-spectra from which the oxygen vacancy concentration can be deduced. It appears that $x = 0.065$—instead of the nominal composition of $x = 0.10$. The isomer shift values for both sites are typical for divalent Fe in the low spin state. At 95 K, both Fe sites are magnetically ordered and the major sub-spectrum was analyzed in terms of an asymmetric Gaussian distribution of magnetic hyperfine fields, with the maximum probability of $H_{eff} \sim 50$ kOe.

Acknowledgments

This research was partially supported by the Israel Science Foundation (ISF, 2004 grant number: 618/04) and by the Klachky Foundation for Superconductivity. The authors from NPL, India, thank their director Professor Vikram Kumar for encouragement.

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