RAPID COMMUNICATIONS

PHYSICAL REVIEW B **80**, 220503(R) (2009)

Coexistence of long-ranged magnetic order and superconductivity in the pnictide superconductor $SmFeAsO_{1-x}F_x$ ($x=0$, 0.15)

D. H. Ryan,[1] J. M. Cadogan,[2] C. Ritter,[3] F. Canepa,[4] A. Palenzona,[5] and M. Putti[6]

[1]*Physics Department and Centre for the Physics of Materials, McGill University, 3600 University Street, Montreal, Quebec, Canada H3A 2T8*

[2]*Department of Physics and Astronomy, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2*

[3]*Institut Laue-Langevin, 156X, 38042 Grenoble Cédex, France*

[4]*CNR-INEM and Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, 16146 Genova, Italy*

[5]*CNR-INFM-LAMIA and Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, 16146 Genova, Italy*

[6]*CNR-INFM-LAMIA and Dipartimento di Fisica, Università di Genova, Via Dodecaneso 33, 16146 Genova, Italy*

(Received 23 October 2009; published 10 December 2009)

Powder neutron-diffraction measurements on both SmFeAsO and the fluorine-doped superconductor, $SmFeAsO_{0.85}F_{0.15}$, show that the Sm sublattice orders magnetically. In both cases we observe a simple layered antiferromagnetic arrangement of the $\sim 0.5\mu_B$ Sm moments. This provides direct evidence that long-ranged magnetic order of the samarium moments coexists with superconductivity in the $SmFeAsO_{1-x}F_x$ system.

DOI: 10.1103/PhysRevB.80.220503 PACS number(s): 74.70.−b, 61.05.F−, 75.50.Ee

I. INTRODUCTION

The recent discovery of the iron-pnictide high-T_c superconducting materials[1–4] has opened a new window onto the physics of unconventional superconductors. While the charge-doping-induced transition to superconductivity exhibits many similarities to the well-studied cuprate systems, many of these newer iron-pnictide materials contain two magnetic elements (Fe and a rare-earth metal) and the interplay between magnetic ordering and superconductivity may be more important here than in the older cuprate systems. Neutron-diffraction measurements on the La,[5] Ce,[6] Pr,[7] and Nd (Ref. 8) systems all show that the magnetic ordering of both the iron and the rare-earth (R) moments seen in the parent RFeAsO compounds is lost on doping before the onset of superconductivity. However, in the $SmFeAsO_{1-x}F_x$ system that exhibits the *highest* superconducting transition temperature (T_c=55 K),[2,9] indirect evidence from heat capacity[10] and muon spin relaxation (μSR) (Ref. 11) suggests that magnetic ordering of the Sm ions coexists with superconductivity over a wide range of compositions. Here, we present the results of a direct search for the magnetic ordering of the Sm moments using thermal neutron diffraction. We find that the $\sim 0.5\mu_B$ Sm moments order antiferromagnetically along the c axis in *both* the parent SmFeAsO and the superconducting $SmFeAsO_{0.85}F_{0.15}$ materials, clearly demonstrating that long-ranged antiferromagnetic Sm order and superconductivity do indeed coexist in this remarkable system.

SmFeAsO adopts the tetragonal ZrCuSiAs-type structure ($P4/nmm$, No. 129) at room temperature and undergoes a tetragonal→orthorhombic transformation at 130 K with $b_o > a_o \sim a_T\sqrt{2}$ and $c_o \sim c_T$ (space group $Cmma$, No. 67).[12] Doping with fluorine to form $SmFeAsO_{1-x}F_x$ gradually suppresses the structural transition and by $x\sim 0.14$ it no longer occurs. μSR (Ref. 13) measurements indicate that the ordering temperature of the iron moments tracks the tetragonal→orthorhombic transition quite closely and, since superconductivity appears near $x=0.07$, Drew *et al.*[13] argued that the magnetic order on the iron sublattice coexists with superconductivity over a wide composition range. More recent μSR data suggest that this coexistence may be more limited in an extent.[14] While a limited coexistence of iron magnetic order with superconductivity may occur near the onset of superconductivity at $x\sim 0.07$, there is strong, albeit indirect, evidence from both heat capacity[10,15] and μSR (Ref. 11) that Sm ordering persists well into the superconducting composition range, at least as far as $x=0.18$. It is the direct search for this Sm ordering using neutron diffraction that is the subject of our study.

II. EXPERIMENTAL METHODS

The two polycrystalline samples used here were prepared in two steps:[16] (1) synthesis of SmAs from the pure elements and (2) synthesis of the final compounds by reacting SmAs with stoichiometric amounts of Fe, Fe_2O_3, and FeF_2 in an evacuated quartz flask at 1200 °C for 24 h to form a cylindrical pellet with a mass of ~3–4 g. The pellet was then ground, repressed, and sintered at 1300 °C for further 72 h. Samples were characterized by x-ray powder diffraction followed by Rietveld refinement to confirm their single-phase highly crystalline nature. TEM analysis showed no structural defects. Both samples used here have undergone an extensive structural and magnetic analysis as part of earlier studies.[17,18] The superconducting transition in our $SmFeAsO_{0.85}F_{0.15}$ sample was measured to be $T_c^{onset}=53.5$ K.[18]

The large thermal neutron absorption cross section for natural samarium (~6000 b, nearly 2.5 times that of cadmium that is commonly used for neutron shielding) makes neutron diffraction work with Sm-based materials rather challenging. The calculated $1/e$ thickness for SmFeAsO is about 80 mg/cm^2, precluding the use of conventional sample holders. We used a recently developed large-area single-crystal flat-plate sample holder[19] to place about 1.6 g of material in the neutron beam. The plate was oriented perpendicular to the beam in order to minimize absorption as the primary scattering of interest was expected to occur at low angles. The scattering measurements were carried out at a wavelength of 2.417 Å on the D20 thermal powder diffractometer located at the Institut Laue-Langevin in Grenoble, France. Sample cooling was achieved using a conventional "orange" He-flow cryostat. For each sample, data sets were obtained at 1.6 and 10.0 K with counting times of 10 h (SmFeAsO) and 15 h ($SmFeAsO_{0.85}F_{0.15}$) for each temperature. The purely nuclear patterns at 10 K [Fig. 1(a)] were fitted to establish scale factors, lattice parameters, and the instrument profile function. These were then fixed while the difference patterns (1.6–10 K) were fitted to obtain the magnetic structure. All refinements of the neutron-diffraction patterns employed the FULLPROF/WINPLOTR suite.[20,21] The complex scattering length for natural samarium at 2.417 Å ($E = 14.0$ meV) was determined by a linear interpolation of data taken from the paper of Lynn and Seeger[22] which yielded $b_{Sm} = (1.13 - 1.26i)$ fm.

III. RESULTS

The difference patterns presented in Figs. 1(b)–1(d) show clear evidence of magnetic ordering. At the temperatures used, the patterns should not be affected by changes in any iron ordering that might be present and so the difference patterns reflect only ordering of the Sm moments. The magnetic signal is extremely weak as the Sm moment is quite modest, and the strongest magnetic peak in Fig. 1(b) [(110) at $2\theta = 35.8°$] is approximately 50 times weaker than the most prominent nuclear reflection in Fig. 1(a) [(002) at $2\theta = 33.2°$]. We emphasize that *all* of the identified magnetic peaks can be indexed to the corresponding crystallographic cell, and none of them overlap with a strong nuclear reflection and so their presence in the difference patterns cannot be attributed to the effects of thermal expansion shifting the peaks. Finally, as we show below, the observed pattern of magnetic reflections corresponds to a simple allowed magnetic structure.

Given the weakness of the magnetic signal, and the limited number of observed magnetic reflections, we restricted our initial analysis to collinear commensurate structures. The Sm atoms are located on the 4*g* site of the *Cmma* space group for SmFeAsO, and the *mm*2 point symmetry of this site only permits ordering along the *a*, *b*, or *c* axis. For a given axis, four ordering modes are permitted, one ferromagnetic and three antiferromagnetic. Magnetization measurements[18] could be used to eliminate the three ferromagnetic modes; however, for completeness they were retained for our analysis. Simulated patterns were calculated for all 12 possible magnetic structures, and only *one* yielded the observed pattern of systematic absences, permitting an unambiguous identification of the magnetic symmetry. The Sm moments order antiferromagnetically along the *c* axis in a *G* mode, which has a $+-+-$ moment sequence [the corresponding atomic positions are $(0\frac{1}{4}z)$, $(0\frac{3}{4}\bar{z})$, $(\frac{1}{2}\frac{3}{4}z)$, and $(\frac{1}{2}\frac{1}{4}\bar{z})$ with $z \sim 0.137$]. In the Shubnikov notation for magnetic space groups, this structure corresponds to the $Cm'm'a'$ group. Figure 2(a) shows a representation of the derived magnetic structure of SmFeAsO at 1.6 K. With the symmetry established, we could proceed to a determination of the Sm moments. Fitting the section of the diffraction pattern shown in Fig. 1(b) yielded a samarium moment of $0.60(3)\mu_B$ for SmFeAsO at 1.6 K. This values compares quite well with the expected moment for the Sm^{3+} ground-state *J* multiplet of $gJ = 0.72\mu_B$. The quoted error is a $1-\sigma$ value that includes only statistical contributions and we would expect the real uncertainty to be somewhat larger.

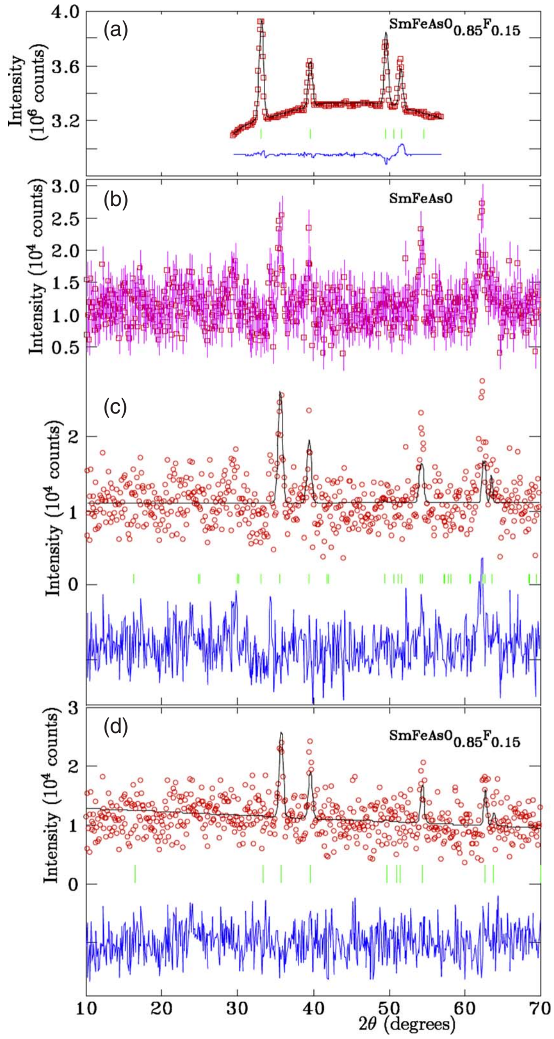

FIG. 1. (Color online) Neutron-diffraction patterns of SmFeAsO and $SmFeAsO_{0.85}F_{0.15}$ measured at a wavelength of 2.417 Å. (a) Nuclear scattering pattern for $SmFeAsO_{0.85}F_{0.15}$ at 10 K used to set scale and profile factors for the magnetic fits. (b) The difference between the 10 and 1.6 K patterns for SmFeAsO shows the new diffraction peaks due to the ordering of the Sm moments. The magnetic signal is approximately 50 times weaker than the nuclear signal due to the small samarium moment. (c) Fitted difference pattern for SmFeAsO using the $Cm'm'a'$ magnetic structure. (d) Fitted difference pattern (10–1.6 K) for $SmFeAsO_{0.85}F_{0.15}$ showing a weak magnetic scattering pattern similar to that seen for SmFeAsO. The solid line shows a fit to the $P4/n'm'm'$ magnetic structure. In each case, where the solid black line shows a fit, Bragg markers (green bars) and residuals (blue line) are given below. The Bragg markers were generated using the reduced symmetry $P\bar{1}$ space group, and most have zero structure factors. They serve to emphasize both the presence and absence of possible reflections.

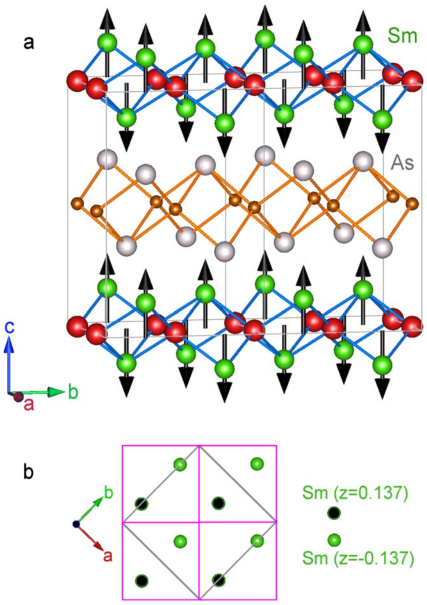

FIG. 2. (Color online) (a) The Sm magnetic structure of SmFeAsO at 1.6 K. The layered nature of both the chemical and magnetic structures is emphasized by showing two unit cells in the *b* direction. (b) A projection of the magnetic structure onto the basal plane shows the relationship between the magnetic structures of SmFeAsO and $SmFeAsO_{0.85}F_{0.15}$ at 1.6 K. The black disks mark the Sm atoms on the $z=0.137$ plane that have their moments pointing "up," while the green (paler) disks denote Sm atoms on the $\bar{z}$ plane that have their moments pointing "down." Four unit cells of the smaller (tetragonal, $P4/nmm$) form of $SmFeAsO_{0.85}F_{0.15}$ each containing two Sm atoms (one each of black and green) are shown by the magenta lines, while the relationship to the larger (orthorhombic, *Cmma*) cell of SmFeAsO that contains four Sm atoms is shown by the gray lines. Note that the orthorhombic basal lattice parameters differ by only 0.7% and cannot be distinguished here.

A similar analysis of the $SmFeAsO_{0.85}F_{0.15}$ data shown in Fig. 1(d) yielded a closely related magnetic structure (Shubnikov magnetic space group $P4/n'm'm'$) and a Sm moment of $0.53(3)\mu_B$ (again, this is a $1-\sigma$ statistical error). The relationship between the crystal and magnetic structures of the two materials studied here is shown in Fig. 2(b). It is important to note that the most significant aspect of the pattern shown in Fig. 1(d) is not that SmFeAsO and $SmFeAsO_{0.85}F_{0.15}$ adopt closely related magnetic structures but, rather, that the Sm moments are *magnetically ordered* in a superconducting sample [recall that this sample exhibits a T_c^{onset} of 53.5 K (Ref. 18)]. Previous neutron-diffraction searches in the corresponding Ce,[6] Pr,[7] and Nd (Ref. 8) systems have all shown that sufficient fluorine doping to yield superconductivity also suppresses the magnetic ordering of the rare-earth moments. It is unlikely that the magnetic ordering observed here reflects a phase separation into superconducting and magnetic regions. Both susceptibility and μSR measurements on several superconducting $SmFeAsO_{1-x}F_x$ samples prepared by us showed bulk superconducting behavior.[14] Attributing the magnetic scattering to a reduced volume fraction of the sample would lead to unphysically large values for the ordered samarium moment. Furthermore, the samarium moment observed in the parent compound (SmFeAsO), where no phase separation could be expected, is essentially the same as that seen in the superconducting $SmFeAsO_{0.85}F_{0.15}$ sample. We therefore conclude that there is a bulk coexistence of superconductivity and long-ranged antiferromagnetic order in $SmFeAsO_{0.85}F_{0.15}$.

It is clear from Fig. 1(b) that the magnetic structure adopted by the Sm moments is quite different from those previously reported in the Ce,[6] Pr,[7] and Nd (Ref. 8) systems. In particular, the (001) reflection at $2\theta \sim 16.4°$ and the (100)/(010) reflections at $2\theta \sim 25.1°$ that dominate the magnetic patterns of the lighter rare-earth compounds are completely absent from that of SmFeAsO in Fig. 1(b). Indeed, it was the absence of these two reflection groups and that of the (101)/(011) group at $2\theta \sim 30.2°$ that allowed us to exclude all but the $Cm'm'a'$ group from consideration as candidate magnetic structures for SmFeAsO. Furthermore, since these absent reflections would occur at *lower* angles than the ones that we actually observe, they would be favored by both the magnetic form factor of Sm and the slightly lower absorption effects in the flat-plate sample: their absence is therefore a robust result that allows us to exclude all but one of the simple magnetic structures considered here and also to exclude the more complex magnetic structures observed in the Ce, Pr, and Nd compounds. Finally, in a very recent analysis of magnetic order in several *R*FeAsO compounds studied using μSR and drawing on some Mössbauer data, a mixed magnetic structure comprising two *c*-axial moments and two basal-plane moments was postulated for the Sm sublattice in SmFeAsO.[23] The fact that we do not observe any magnetic scattering at either the (100)/(010) or the (101)/(011) positions again allows us to rule out this proposed magnetic structure.

It is interesting to note that the magnetic structure of SmFeAsO (ferromagnetic *ab* planes ordered antiferromagnetically along the *c* axis, with the Sm moments parallel to the *c* axis) is essentially the same as that adopted by the Sm moments in Sm_2CuO_4,[24] and that both compounds exhibit an unusual insensitivity of T_N^{Sm} to an externally applied magnetic field. In Sm_2CuO_4 (Ref. 25) the field shift is ~13 mK/T, while in SmFeAsO it is ~19 mK/T.[15] This should be contrasted with the ~160 mK/T shift seen in CeFeAsO where even 5 T is sufficient to almost completely suppress the heat capacity feature at T_N^{Ce}.[15]

It is not clear yet why samarium ordering coexists with superconductivity in $SmFeAsO_{0.85}F_{0.15}$ and what role the robust Sm-Sm exchange plays in setting the high superconducting transition temperatures seen in this series. However, direct studies of the magnetic ordering and excitations in these remarkable pnictide superconductors will certainly be needed if progress is to be made.

IV. CONCLUSIONS

We have carried out a direct search for magnetic ordering of the samarium moments in the $SmFeAsO_{1-x}F_x$ system using thermal neutron diffraction. Our results for SmFeAsO and $SmFeAsO_{0.85}F_{0.15}$ show that in both cases the Sm moments exhibit long-ranged antiferromagnetic order at 1.6 K, and that the magnetic order of the Sm moments *coexists* with superconductivity in $\mathrm{SmFeAsO_{0.85}F_{0.15}}$. This remarkable bulk coexistence appears to be unique to the $\mathrm{SmFeAsO_{1-x}F_x}$ system. Furthermore, the ordered Sm moments in both the undoped and superconducting materials are essentially the same $[0.60(3)\mu_B$ and $0.53(3)\mu_B$, respectively$]$ so there is no evidence that the ordering is in any way weakened by the doping that leads to the onset of superconductivity.

ACKNOWLEDGMENTS

Financial support for various stages of this work was provided by the Natural Sciences and Engineering Research Council of Canada and Fonds Québécois de la Recherche sur la Nature et les Technologies. J.M.C. acknowledges support from the Canada Research Chairs Program. The support of the technical and scientific staff at the Institut Laue-Langevin in Grenoble is gratefully acknowledged.

---

[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).

[2] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature (London) **453**, 761 (2008).

[3] G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, Phys. Rev. Lett. **100**, 247002 (2008).

[4] Z.-A. Ren *et al.*, EPL **83**, 17002 (2008).

[5] Q. Huang, J. Zhao, J. W. Lynn, G. F. Chen, J. L. Luo, N. L. Wang, and P. Dai, Phys. Rev. B **78**, 054529 (2008).

[6] J. Zhao *et al.*, Nature Mater. **7**, 953 (2008).

[7] J. Zhao *et al.*, Phys. Rev. B **78**, 132504 (2008).

[8] Y. Qiu *et al.*, Phys. Rev. Lett. **101**, 257002 (2008).

[9] K. Ishida, Y. Nakai, and H. Hosono, J. Phys. Soc. Jpn. **78**, 062001 (2009).

[10] L. Ding, C. He, J. K. Dong, T. Wu, R. H. Liu, X. H. Chen, and S. Y. Li, Phys. Rev. B **77**, 180510(R) (2008).

[11] A. J. Drew *et al.*, Phys. Rev. Lett. **101**, 097010 (2008).

[12] S. Margadonna, Y. Takabayashi, M. T. McDonald, M. Brunelli, G. Wu, R. H. Liu, X. H. Chen, and K. Prassides, Phys. Rev. B **79**, 014503 (2009).

[13] A. J. Drew *et al.*, Nature Mater. **8**, 310 (2009).

[14] S. Sanna, R. De Renzi, G. Lamura, C. Ferdeghini, A. Palenzona, M. Putti, M. Tropeano, and T. Shiroka, Phys. Rev. B **80**, 052503 (2009).

[15] S. Riggs, C. Tarantini, J. Jaroszynski, A. Gurevich, D. Larbalestier, A. Palenzona, M. Putti, T. Duc Nguyen, and M. Affronte, arXiv:0909.3625 (unpublished).

[16] A. Martinelli *et al.*, Supercond. Sci. Technol. **21**, 095017 (2008).

[17] A. Martinelli, A. Palenzona, C. Ferdeghini, M. Putti, and H. Emerich, J. Alloys Compd. **477**, L21 (2009).

[18] M. R. Cimberle, F. Canepa, M. Ferretti, A. Martinelli, A. Palenzona, A. S. Siri, and C. Tarantini, J. Magn. Magn. Mater. **321**, 3024 (2009).

[19] D. H. Ryan and L. M. D. Cranswick, J. Appl. Crystallogr. **41**, 198 (2008).

[20] J. Rodríguez-Carvajal, Physica B **192**, 55 (1993).

[21] T. Roisnel and J. Rodríguez-Carvajal, Mater. Sci. Forum **378-381**, 118 (2001).

[22] J. E. Lynn and P. A. Seeger, At. Data Nucl. Data Tables **44**, 191 (1990).

[23] H. Maeter *et al.*, Phys. Rev. B **80**, 094524 (2009).

[24] I. W. Sumarlin, S. Skanthakumar, J. W. Lynn, J. L. Peng, Z. Y. Li, W. Jiang, and R. L. Greene, Phys. Rev. Lett. **68**, 2228 (1992).

[25] T. Holubar, G. Schaudy, N. Pillmayer, G. Hilscher, M. Divis, and V. Nekvasil, J. Magn. Magn. Mater. **104-107**, 479 (1992).