Neutron scattering investigation of the magnetic order in single crystalline BaFe$_2$As$_2$

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Abstract. The magnetic structure of BaFe$_2$As$_2$ was determined from polycrystalline neutron diffraction measurements soon after the ThCr$_2$Si$_2$-type FeAs-based superconductors were discovered. Both the moment direction and the in-plane antiferromagnetic wavevector are along the longer $a$-axis of the orthorhombic unit cell. There is only one combined magnetostructural transition at $\sim$140 K. However, a later single-crystal neutron diffraction work reported contradicting results. Here, we show neutron diffraction results from a single-crystal sample, grown by a self-flux method, that support the original polycrystalline work.
1. Introduction

Over the last two years, several superconductors have been discovered in fluorine-doped lanthanum oxypnictides LaFePO [1], LaNiPO [2] and LaFeAsO [3]. The common ZrCuSiAs-type (1111) structure is composed of alternating Fe(Ni)As(P) and LaO layers. Band structure calculations indicate that electronic states at the Fermi level are contributed predominately by the transition metal Fe or Ni in these semimetals [4]–[9], thus the importance of the layer formed by the edge-sharing Fe(Ni) pnictide tetrahedra. The same edge-sharing tetrahedral layer is also the central structural component in the previously discovered LnNi2B2C superconductors [10]. However, a distinguishing feature of the LaFeAsO system is that its superconducting transition temperature $T_C$ increases from 26 K to above 40 K [11, 12], and finally reaches about 55 K at optimal F doping [13, 14] when La is replaced by the magnetic Sm or Ce. Other magnetic lanthanide substitutions have also been shown to result in increased $T_C$ [15]–[22]. Therefore, an unconventional superconducting mechanism is suspected. Indeed while the FeP and NiP materials with their low-$T_C \approx 3–4$ K may be accounted for by conventional electron–phonon interactions, the $T_C$ of the FeAs materials is too high for the phonon mechanism according to theoretical calculations [23]. The first-principle phonon spectrum used in the calculations has found support from neutron scattering, optical and resonant x-ray scattering measurements [24]–[28].

While the LnO layer ($Ln = La, Sm, Ce, Nd, Pr, Gd, Tb$ or Dy [3], [11]–[22]) provides an excellent opportunity to investigate the interaction between the superconductivity and rare-earth magnetism in the LnFeAsO systems, its existence is not necessary for superconductivity. Superconductivity has been discovered in related materials with the ThCr2Si2-type (122) structure, where the LnO layer is replaced by an elemental Ba [29], Sr [30, 31] or Ca [32] layer, and in Li$_{1+x}$FeAs [33] and Fe$_{1+x}$(Se, Te) [34, 35] with the PbO-type (11) structure, which does not contain the intervening layer, but Li [36] or excess Fe [37] occupies an interstitial site. Therefore, the multiorbital theoretical model based on similar semimetallic electronic states from the common Fe structural layer is likely to capture the essential physics for understanding high-$T_C$ superconductivity in these Fe-based materials [38]–[46]. In addition, magnetic fluctuations have been proposed as the bosonic glue for Cooper pair formation. Currently, the extended s-wave superconductivity mediated by magnetic fluctuations is favored. Experiments supporting a nodeless superconducting gap have emerged [47]–[49].

Stoichiometric LnFeAsO and $AFe_2As_2$ ($A = Ba, Sr$ or Ca) are not superconductors. LaFeAsO experiences a structural transition from tetragonal to orthorhombic symmetry at 150 K, which shows up as a strong anomaly in resistivity, and an antiferromagnetic transition
at 137 K [50, 51]. For BaFe$_2$As$_2$, the structural and magnetic transitions occur at the same temperature [52]. The magnetic propagation vector is $(\pi, 0, \pi)$ in terms of the primitive tetragonal magnetic unit cell for both LaFeAsO [50, 53] and BaFe$_2$As$_2$ [52], although their crystal structures are different. When La is replaced by magnetic Nd or Pr, the magnetic wavevector changes to $(\pi, 0, 0)$ in the combined Fe and rare-earth magnetic order at low temperature [54]–[56]. For Ce substitutions, a different antiferromagnetic ordering of Ce ions was reported without the refinements provided [57], but the Fe part of the magnetic order is still the same as we reported for the Nd compound and is characterized by $(\pi, 0, 0)$ [54].

The in-plane $(\pi, 0)$ magnetic wavevector is consistent with the nesting of electron and hole Fermi surfaces, which has been anticipated from band structure theory [39, 58, 59]. It breaks the tetragonal symmetry of the high-temperature structure and is consistent with the orthorhombic distortion at low temperature. The antiparallel moment alignment is determined by neutron diffraction to be along the longer of the in-plane axes and the parallel alignment along the shorter axis of the orthorhombic unit cell in both NdFeAsO and BaFe$_2$As$_2$ [52, 54]. This magnetostriction pattern is opposite to the usual case of single orbital magnetism and is explained by careful calculations taking into account the multiorbital origin of the antiferromagnetic order [60]. The moment direction has also been determined to be along the longer of the in-plane axes [52, 54]. The same magnetostrictive expansion and contraction have been found later in SrFe$_2$As$_2$ [61, 62], CaFe$_2$As$_2$ [63] and PrFeAsO [55, 56] in poly- and single-crystal studies. However, in a single-crystal neutron diffraction study of BaFe$_2$As$_2$ [64], results different from our polycrystalline work [52] have been reported. To clarify the issue, we show single-crystal results in section 3, which are consistent with our previous polycrystalline study.

### 2. Experimental details

The single-crystal sample of BaFe$_2$As$_2$ was grown using a self-flux method [65]. A distinct feature of single crystals grown this way is that the resistivity shows a sharp drop at the phase transition at $\sim$140 K, similar to the results from polycrystalline samples. The single crystal used by Su et al in their single-crystal neutron diffraction work was grown in Sn flux [64]. Not only is the transition temperature much reduced, but also the material becomes an insulator at low temperature, in contrast to the expected metallic behavior. We conducted single-crystal neutron diffraction measurements with the cold neutron triple-axis spectrometer SPINS at the NIST Center for Neutron Research. The sample was mounted in a He-filled Al can in a closed cycle refrigerator so that $(h0l)$ was in the scattering plane. Neutrons of 5 meV were selected using pyrolytic graphite (002) as both monochromator and analyzer. A cold Be filter was placed in the neutron path to reduce contamination from higher order neutrons. The lattice parameters are $a = 5.615$, $b = 5.571$ and $c = 12.97$ Å at 12.5 K in the orthorhombic structure.

### 3. Single-crystal diffraction experiments

The mosaic of our BaFe$_2$As$_2$ single-crystal sample is shown in figure 1(b). The composition uniformity is indicated by the nice peak in the $\theta$–$2\theta$ scan in figure 1(a). At 12.5 K, the orthorhombic distortion of the crystal structure is indicated by the well resolved $(400)$ and $(040)$ Bragg peaks due to twinning in figure 1(c). That $a > b$ is reflected in the shorter reciprocal length of the $|400|$ in comparison with $(040)$. The fact that only $(101)$, not the twinning $(011)$, peak exists in figure 1(d) is consistent with our previous determination of the $(101)$, not
Figure 1. (a, b) The $\theta$–$2\theta$ and rocking scans of the (004) structural Bragg peak. (c) The twinning (400) and (040) structural Bragg peaks measured using $\lambda/2$ neutrons near the (200) position. (d, e) Two perpendicular scans through the (101) magnetic Bragg peaks. (f) The (103) magnetic Bragg peak. The blue symbols represent measurements at 12.5 K and the red at 150 K. The error bars in all the figures represent the standard deviation in the measurement.

(011), as the magnetic propagation vector with the definition of $a > b$ [52]. This is opposite to what was reported by Su et al for their Sn-flux grown single-crystal sample [64]. The $l$ scan in figure 1(e), close to the rocking direction, further supports the commensurate assignment of the magnetic propagation vector.

Consistent with our previous data [52], the (103) magnetic Bragg peak in figure 1(f) is stronger than that of (101), reflecting the moment orientation factor in the magnetic neutron diffraction cross section when the moment points along the (100)-direction. At 150 K above the simultaneous magnetostructural transition, magnetic Bragg peaks disappear completely as shown in figure 1(d) for (101).

While there is no dispute regarding the first-order nature of the structural transition in BaFe$_2$As$_2$ [52], the continuous appearance of the magnetic order parameter raises a scenario where the magnetic transition is of second-order. If so, the lack of hysteresis in the presumed second-order magnetic transition would indicate two-phase transitions during a cooling/heating cycle, since obvious hysteresis in the structural transition has been observed, suggesting a similar situation to the double transition case of LaFeAsO [51]. However, a continuous appearance of the magnetic order parameter does not preclude a magnetic transition with first-order hysteresis. This has been shown previously to occur in Ca$_3$Ru$_2$O$_7$ in a wide phase space of the temperature-magnetic field plane [66], where there exists a lattice contraction associated with a Mott transition. This has also been demonstrated for CaFe$_2$As$_2$ [63], verifying that there is indeed only one simultaneous magnetic and structural transition in the 122 materials. In figure 2, the squared magnetic order parameter is shown during the cooling and warming.

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Figure 2. Temperature dependence of the magnetic (101) Bragg peak as a measure of the squared magnetic order parameter. The blue symbols were measured during cooling and the red during heating. The temperature ramping rate was $2.3 \text{ K min}^{-1}$ for $\bullet$, and $4.5 \text{ K min}^{-1}$ for $\circ$.

cycle for the BaFe$_2$As$_2$ single-crystal sample. The small difference between measurements using the two ramping rates indicates the rate is slow enough. A supercooling of about 20 K was observed, which is twice that observed previously for the polycrystalline sample [52]. This larger hysteresis in the single crystal sample is expected due to larger structural strain being dissipated in the single crystal at the first-order transition.

4. Discussions

Using a single-crystal sample of BaFe$_2$As$_2$ grown by a self-flux method, the original magnetic structure determined using a polycrystal sample [52] is confirmed. The single-crystal sample used by Su et al has very different physical properties, likely due to inclusion of the Sn flux in the crystal. It is not clear whether the Sn inclusion is also responsible for the very different magnetic structure reported by them. Their sample also showed decoupled magnetic and structural transitions, and the orthorhombic distortion survived at high temperature in the heating cycle. This is different from our poly and now also single crystal results. Note that except for the results reported by Su et al, magnetic and structural properties of the Ba, Sr and Ca 122 materials are very similar.

The prediction of the $(\pi, 0)$ in-plane magnetic wavevector from the nesting of the quasi-two-dimensional Fermi surface before experiments [39, 58, 59] certainly has boosted the credential of the spin density wave (SDW) mechanism for antiferromagnetism discovered in both the 1111 and 122 materials. The same SDW prediction for Fe$_{1+y}$Te [67], however, differs from our observed magnetic structure characterized by a completely different magnetic propagation vector $(\delta\pi, \delta\pi, \pi)$ with $\delta$ tunable from 0.346 to 0.5, namely from incommensurate...
to commensurate magnetic structures, by excess Fe composition [37]. In addition, the customary energy gap from SDW order is absent in angle-resolved photoemission spectroscopy (ARPES) measurements [68]. A possible cause due to a topological constraint of degenerate orbitals has been advanced theoretically [69]. On the other hand, there has been another theoretical approach from the strong correlation side which explains magnetic order in the Fe-based materials from a localized magnetic moment picture [60, 70]. Both localized and itinerant theories now exist for Fe$_{1+x}$Te [9, 71, 72], and incommensurate magnetic order is also possible from either localized or itinerant perspectives [60, 73]. Nevertheless, the strength of electronic correlations may lie in between the weak and strong correlation limits in the ferrous high-$T_c$ superconductors, since the electronic band structure measured by ARPES shows certain departures from the LDA band structure [48, 49, 68, 74].

5. Summary

We have performed a single-crystal neutron diffraction study on BaFe$_2$As$_2$. The results are completely consistent with those from our original work using a polycrystalline sample [52]. Despite the appearance of a continuous magnetic order parameter, there is only one combined magnetostructural first-order transition in BaFe$_2$As$_2$. The conflicting results reported by Su et al using an Sn-flux grown single-crystal sample most likely erroneously represent the intrinsic properties of BaFe$_2$As$_2$.

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