

## Origin of the dynamics of the spin state in undoped $\text{BaFe}_2\text{As}_2$ : Mössbauer studies

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2011 J. Phys.: Condens. Matter 23 342201

(<http://iopscience.iop.org/0953-8984/23/34/342201>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 146.201.213.179

The article was downloaded on 16/08/2011 at 17:09

Please note that [terms and conditions apply](#).

## FAST TRACK COMMUNICATION

# Origin of the dynamics of the spin state in undoped $\text{BaFe}_2\text{As}_2$ : Mössbauer studies

Airat Khasanov<sup>1</sup>, Jianyi Jiang<sup>2</sup>, Eric E Hellstrom<sup>2</sup> and Amar Nath<sup>1</sup><sup>1</sup> Department of Chemistry, University of North Carolina, Asheville, NC 28804, USA<sup>2</sup> Applied Superconductivity Center, National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USAE-mail: [anath@unca.edu](mailto:anath@unca.edu)

Received 20 June 2011, in final form 14 July 2011

Published 12 August 2011

Online at [stacks.iop.org/JPhysCM/23/342201](http://stacks.iop.org/JPhysCM/23/342201)**Abstract**

Fe–As based superconductors provide a good system for understanding the relationship between magnetism and superconductivity. Considerable efforts have been expended in understanding the magnetic behavior of the parent compound,  $\text{BaFe}_2\text{As}_2$ . However, it had not been realized that traces of adsorbed  $\text{O}_2$  by the material bring about drastic changes in its magnetic behavior.  $\text{O}_2$  is known to trap electrons, forming  $\text{O}_2^-$ . Guided by this discovery, we observe in the absence of  $\text{O}_2$  a dynamic transition between intermediate and low spin states of Fe and hysteresis effects, and in the presence of  $\text{O}_2$  trapping of the magnetic state. These observations are likely to have a bearing on the role of magnetism in superconductivity.

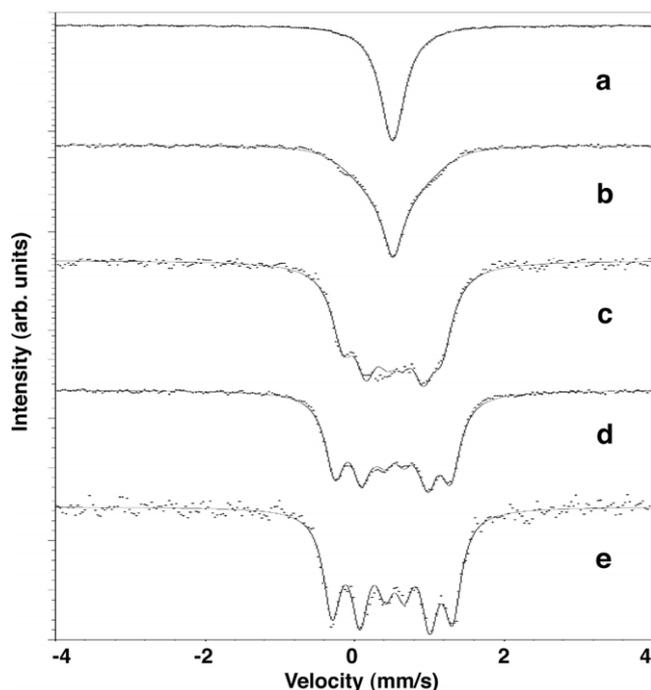
The Fe–As based superconductors are currently attracting a great deal of attention because of their unconventional behavior. In the 122 family,  $\text{BaFe}_2\text{As}_2$  is the parent compound, where the iron atoms are arranged in a planar square with each one coordinated tetrahedrally to four As atoms resulting in layers of edge-sharing tetrahedra. Ba ions are sandwiched between the Fe–As layers. When Fe is substituted by a few per cent of a transition element like Co or Ni, it exhibits superconductivity [1–4]. It is generally believed that the electron(s), donated by the substituents, induce the superconductivity. The undoped compound has a tetragonal structure and exhibits paramagnetic behavior at room temperature. On lowering the temperature it changes to orthorhombic structure at  $\sim 140$  K with antiferromagnetic alignment of the Fe spins. It seems that there is considerable orbital-dependent reconstruction of the electronic configuration across the magnetostructural transition [4–6]. Therefore, unsurprisingly several groups carrying out Mössbauer measurements have observed a singlet at room temperature, characteristic of a paramagnetic compound, and a magnetically split sextet at low temperatures [5, 8–15]. The magnetism is centered on the Fe and not on the Ba or As. However, the origin of magnetism and its weakness have led to considerable discussion and

controversy [6, 7]. It is generally believed that the Fe–As based superconductors do not exhibit the phonon-mediated Bardeen–Cooper–Schrieffer pairing mechanism. In view of the above, the role of magnetism in mediating pair formation is currently being hotly debated [2, 3, 6]. In short, it is essential that we fully understand the nature of the magnetism in the parent compound,  $\text{BaFe}_2\text{As}_2$ .

Our studies reported in this communication bear on the magnetic behavior in the orthorhombic phase of the parent compound. We find that a strong influence of adsorbed oxygen (air) on the material and other defects in the solid are responsible for masking the nature of the spin states of Fe, namely intermediate and low spins, and their dynamics.

The reported investigations are based on observations made on two polycrystalline lots of  $\text{BaFe}_2\text{As}_2$  prepared at FSU. They were characterized by x-ray diffraction and energy dispersive x-ray analysis (EDX) measurements. Mössbauer measurements were made on powdered materials using a  $^{57}\text{Co}(\text{Rh})$  source. A closed cycle ARS (Advanced Research Systems) cryostat was used for recording the spectra at specified temperatures.

At 90 K, for an atmospheric pressure of 1 mTorr or lower, one observes a singlet and it gradually transforms to a fully developed sextet at higher pressures (figure 1). Interestingly,

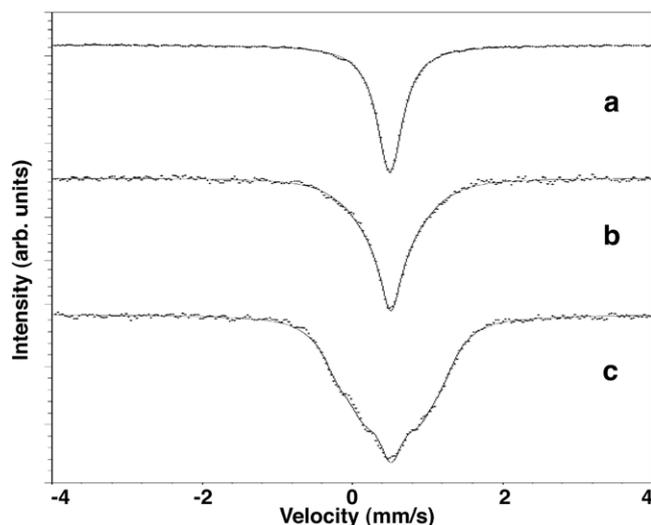


**Figure 1.** Mössbauer spectra of  $\text{BaFe}_2\text{As}_2$  at  $T = 90$  K and different atmospheric pressures: 1 mTorr (a), 35 mTorr (b), 40 mTorr (c), 160 mTorr (d), 750 Torr (e).

the behavior at each step is completely reversible at 90 K. In the near absence of  $\text{O}_2$  the rate of fluctuation is very high and a singlet is observed (figure 1(a)); the rate decreases gradually and finally adsorbed  $\text{O}_2$ , which is known to be an effective electron acceptor forming  $\text{O}_2^-$  (e.g. [16]), completely traps the magnetic state. At lower pressures, a limited amount of oxygen permeates the material forming small sized spin clusters (magnetic polarons) resulting in superparamagnetic like behavior. Spectra (a) and (b) in figure 1 arise when the thermal energy,  $kT$ , is sufficient to flip the magnetization vector of the small spin clusters among the two easy directions at a rate comparable to or faster than the Larmor frequency of the daughter  $^{57}\text{Fe}$  ( $\sim 10^7 \text{ s}^{-1}$ ) which results in a zero or near zero field at the  $^{57}\text{Fe}$  nuclei. When a larger amount of  $\text{O}_2$  is available, the size of the spin clusters grows and they cannot fluctuate at a fast rate with the thermal energy available at 90 K. In addition, the magnitude of the hyperfine magnetic field increases with the size of the spin clusters from 41 kOe, through 48–50 kOe (figure 1(c)–(e)).

Surprisingly if the  $\text{O}_2$  is not desorbed at a higher temperature like 90 K by pumping, one continues to observe a resolved sextet at lower temperatures. The literature is replete with observations of well resolved sextets for several other 122 compounds of the form  $\text{REFe}_2\text{As}_2$  also, where  $\text{RE} = \text{Eu}, \text{Sr}$  or  $\text{Ca}$ , presumably because of traces of adsorbed  $\text{O}_2$  (e.g. [5, 8–15]).

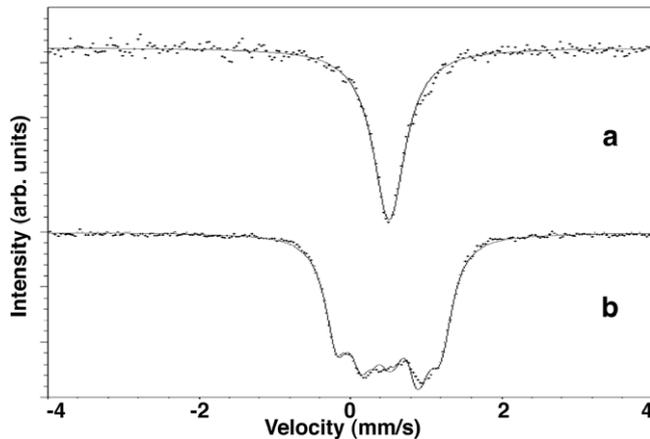
In a sample under high vacuum, we observed a singlet at 90 K depicting very rapid relaxation of spin states with a frequency of  $\geq 10^7 \text{ s}^{-1}$  and the rate slows down through 60 K with frequency  $5.2 \times 10^6 \text{ s}^{-1}$  and to 6 K with frequency  $1.5 \times 10^6 \text{ s}^{-1}$  (figure 2). Therefore (b) and (c) exhibit partially relaxed sextets.



**Figure 2.** Mössbauer spectra of  $\text{BaFe}_2\text{As}_2$  at low atmospheric pressure  $P < 1$  mTorr.  $T = 90$  K (a),  $T = 60$  K (b),  $T = 6$  K (c).

We also observe a very interesting hysteresis behavior. For a sample cooled to 6 K we observe a singlet, which after 48 h converts into a resolved sextet (figure 3). The singlet arises because of the very rapid fluctuations between the intermediate and low spin states. After some duration, the intermediate spin state is trapped, presumably by some defects. This behavior is observed only for one of the preparations. It appears that the magnetic behavior at low temperatures is determined not only by adsorbed  $\text{O}_2$  but also by the nature of intrinsic defects in the material and ones created by grinding. Therefore the behavior can vary somewhat from preparation to preparation. Single crystals, which were shattered gently, also exhibited qualitatively similar behavior to the polycrystalline preparation. The role of defects is also obvious from observations made by Ran *et al* [17] for a crystal of  $\text{CaFe}_2\text{As}_2$  quenched from a high temperature of  $960^\circ\text{C}$ : the Mössbauer spectrum at 5 K exhibits no change from that observed at 295 K and the sextet is conspicuously absent and the singlet survives.

In summary, we observe trapping of spin states by adsorbed oxygen, which constitutes a very good electron trap [16], and other defects, pre-existing or formed by grinding, and strong hysteresis effects. All the observed features are typical for spin-crossover for Fe(II) complexes in the solid state [18–20]. Therefore we can safely conclude that we are observing the dynamics of two spin states of Fe(II) in  $\text{BaFe}_2\text{As}_2$ , namely the intermediate spin state and the low spin state. The singlet at 90 K in good vacuum should be interpreted as fast fluctuations between the two spin states; with increase in air (oxygen) pressure the rate of fluctuations decreases and finally at a higher partial pressure of  $\text{O}_2$  the intermediate spin state exhibiting a sextet is frozen (figure 1). The rate of fluctuations also decreases with temperature for a sample under relatively high vacuum at 90 K and going down to 6 K (figure 2). At lower temperatures, one would normally expect the low spin state to be stabilized. However, the situation is complicated by the role of defects and the low



**Figure 3.** Mössbauer spectra of BaFe<sub>2</sub>As<sub>2</sub> at  $T = 6$  K after 1 h (a), and after 48 h (b).

spin state after 48 h converts into the intermediate spin state exhibiting a sextet (figure 3).

In conclusion, we have demonstrated that in the orthorhombic phase there is dynamic fluctuation between two spin states, namely the intermediate spin and low spin states of Fe in BaFe<sub>2</sub>As<sub>2</sub>. The rate of fluctuation decreases with temperature as expected. The very interesting role of defects and adsorbed O<sub>2</sub> needs to be explored further and also their ramifications for superconductivity in Fe–As based materials.

AN and AK gratefully acknowledge support from NSF DMR-MRI 0922735. JJ and EEH are grateful to Jeremy Weiss for his help with sample preparation. The work at NHMFL was supported by NSF DMR-1006584, NSF DMR-0084173 and by the State of Florida.

## References

- [1] Mandrus D, Sefat A S, McGuire M A and Sales B C 2010 *Chem. Mater.* **22** 715
- [2] Paglione J and Greene R L 2010 *Nature Phys.* **6** 645
- [3] Wang F and Lee D H 2011 *Science* **332** 200
- [4] Kasinathan D, Ormeci A, Koch K, Burkhardt U, Schnelle W, Leithe-Jasper A and Rosner H 2009 *New J. Phys.* **11** 025023
- [5] Rotter M, Tegal M, Johrendt D, Schellenberg I, Hermes W and Pöttgen R 2008 *Phys. Rev. B* **78** 020503
- [6] Lumsden M D and Christianson A D 2010 *J. Phys.: Condens. Matter* **22** 203203
- [7] Shimojima T *et al* 2010 *Phys. Rev. Lett.* **104** 057002
- [8] Bonville P, Rullier-Albenque F, Colson D and Forget A 2010 *Eur. Phys. Lett.* **89** 67008
- [9] Nowik I, Felner I, Ni N, Bud'ko S L and Canfield P C 2010 *J. Phys.: Condens. Matter* **22** 355701
- [10] Khasanov A, Bhargava S C, Stevens J G, Jiang J, Weiss J D, Hellstrom E E and Nath A 2011 *J. Phys.: Condens. Matter* **23** 202201
- [11] Raffius H, Mörsen E, Mosel B, Müller-Warmuth W, Jeitschko W, Terbüchte L and Vomhof T 1993 *J. Phys. Chem. Solids* **54** 135
- [12] Tegal M, Rotter M, Weiss V, Schappacher F M, Pöttgen R and Johrendt D 2008 *J. Phys.: Condens. Matter* **20** 45220
- [13] Alzamora M, Munevar J, Baggio-Saitovitch E, Bud'ko S L, Ni N, Canfield P C and Sanchez D R 2011 *J. Phys.: Condens. Matter* **23** 145701
- [14] Nowik I, Felner I, Ren Z, Cao G H and Xu Z A 2011 *J. Phys.: Condens. Matter* **23** 065701
- [15] Blachowski A, Ruebenbauer K, Zukrowski J, Rogacki K, Bukowski Z and Karpinski J 2011 *Phys. Rev. B* **83** 134410
- [16] Chechersky V, Kopelev N S, B-h O, Larkin M L, Peng J L, Markert J T, Greene R L and Nath A 1993 *Phys. Rev. Lett.* **70** 3355
- [17] Ran S *et al* 2011 *Phys. Rev. B* **83** 144517
- [18] Haddad M S, Federer W D, Lynch M W and Hendrickson D N 1981 *Inorg. Chem.* **20** 131
- [19] Adler P, Hauser A, Vef A, Spiering H and Gütlich P 1989 *Hyperfine Interact.* **47** 343
- [20] Toftlund H 1989 *Coord. Chem. Rev.* **94** 67