Mössbauer studies of the superconducting cobalt/nickel-doped BaFe$_2$As$_2$. Whither go the injected electron(s)?

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

2011 J. Phys.: Condens. Matter 23 202201

(http://iopscience.iop.org/0953-8984/23/20/202201)

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 04/05/2011 at 20:59

Please note that terms and conditions apply.
Mössbauer studies of the superconducting cobalt/nickel-doped BaFe$_2$As$_2$. Whither go the injected electron(s)?

Airat Khasanov$^1$, Satish C Bhargava$^1$, John G Stevens$^1$, Jianyi Jiang$^2$, Jeremy D Weiss$^2$, Eric E Hellstrom$^2$ and Amar Nath$^{1,3}$

$^1$ Department of Chemistry, University of North Carolina, Asheville, NC 28804, USA
$^2$ Applied Superconductivity Center, National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA

E-mail: anath@unca.edu

Received 4 February 2011, in final form 15 March 2011
Published 4 May 2011
Online at stacks.iop.org/JPhysCM/23/202201

Abstract
Mössbauer studies of cobalt- and nickel-doped BaFe$_2$As$_2$ show that the s-electron density at the $^{57}$Fe nuclei, as measured by the isomer shift, is the same as that for the parent BaFe$_2$As$_2$. Apparently, the electron population of the d shell, which shields the s-electron density at the nuclei, remains unchanged. We invoke the involvement of p-orbital hybridization with the d orbital in Fe–As bonding. Furthermore, the shrinkage of the lattice on substitution enhances the As–As sp hybridization, providing a path for the migration of additional electrons. The proposed mechanism is consistent with Hall coefficient and thermoelectric effect measurements.

1. Introduction
The discovery of superconductivity in Fe–As-based compounds in early 2008 by Kamihara et al [1] has generated much interest as is evident from the hundreds of publications and several review articles [2–5]. In the parent compound BaFe$_2$As$_2$, the Fe atoms are arranged in a planar square and each one is coordinated tetrahedrally to four As ions, resulting in layers of edge-sharing slightly distorted tetrahedra. Ba ions are sandwiched between Fe–As layers. At room temperature, BaFe$_2$As$_2$ acquires a tetragonal structure and exhibits paramagnetic behavior. On cooling, it changes to orthorhombic structure at 140 K with antiferromagnetic alignment of Fe spins in the $ab$ plane. It is believed that there is considerable orbital-dependent reconstruction of the electronic structure across the magnetostructural transition in pnictides [6–8].

Fe in BaFe$_2$As$_2$ has been substituted by several transition metals including Co, Ni, Cu, Mn, Cr and Ba by K [2–4, 8–18]. The observed relationship between Co and Ni is particularly interesting. Ni with an additional electron to contribute to the band is found to be twice as effective as Co in inducing superconductivity. Measurements of the Hall coefficient and thermoelectric effect exhibit clear evidence for increased injected electron density [3, 4, 12–14, 17]. On the other hand, substitution of Cu failed to induce superconductivity. Again, K substitution of Ba induced superconductivity due to hole injection. However, Mn and Cr substitution for Fe failed to do so. Interestingly, the isovalent substitution of Ru for Fe [19] and P for As [20, 21] induces superconductivity. It seems that the origin of superconductivity due to substitution of Co, Ni and K is not purely electronic; some other features like Fe–As bond lengths and As–Fe–As bond angles are also involved, among other hitherto unknown features.

2. Experimental details
The polycrystalline materials were prepared at Florida State University (FSU), where Ba, Fe, Ni (or Co) and As were mixed together, and wrapped with Nb foil, and then sealed in...
Figure 1. X-ray diffractogram of polycrystalline Ba\((Fe_{0.95}Ni_{0.05})_2As_2\).

Figure 2. Magnetic susceptibility \(\chi\) of polycrystalline sample of Ba\((Fe_{0.91}Co_{0.09})_2As_2\). (This figure is in colour only in the electronic version)

Figure 3. Mössbauer spectra of BaFe\(_2\)As\(_2\).

Figure 4. Mössbauer spectra of Ba\((Fe_{0.91}Co_{0.09})_2As_2\) and Ba\((Fe_{0.95}Ni_{0.05})_2As_2\) at \(T = 78\) K. The line for Ni-doped material is much narrower than that reported in [22].

We used \(^{57}\)Co\(\text{Rh}\) as the Mössbauer source for transmission mode spectroscopy. Pieces of the material were powdered and sandwiched between plastic discs. The Mössbauer spectrum for pristine BaFe\(_2\)As\(_2\) shows a single line at room temperature and a magnetically split sextet at low temperatures as expected (figure 3). On the other hand, Co- and Ni-doped materials exhibit a single line at 78 K and ambient temperature. The observed Mössbauer parameters for BaFe\(_2\)As\(_2\) and Ni-doped material, obtained by the least-squares fitting procedure, are in concordance with the ones reported in the literature for BaFe\(_2\)As\(_2\) and Ba\((Fe_{0.946}Ni_{0.054})_2As_2\) [8, 22]. Remarkably, the spectra of Co- and Ni-doped materials are almost identical and show no change in the Mössbauer isomer shift due to doping of the parent compound BaFe\(_2\)As\(_2\) (figure 4 and table 1). We attempt to rationalize this enigmatic observation by invoking the involvement of p-orbital rehybridization for Fe–As and As–As bonding.

3. Discussion and conclusions

Mössbauer isomer shifts are sensitively dependent on the s-electron density at the \(^{57}\)Fe nuclei, which is determined by the nature of hybridization of its s orbitals and by shielding of the s electrons by the electron population in its d shell. If electrons are injected into the d shell with consequent enhanced
shielding and a decrease in s-electron density at the $^{57}$Fe nuclei, then one would expect an increase in the isomer shift. Contrary to this, we find that the isomer shifts for the compounds with Co and Ni substitutions are the same as the isomer shift observed for the pristine BaFe$_2$As$_2$ (table 1). Similarly, one should expect the isomer shift to decrease with hole injection. Reviewing the earlier literature, Kitao et al [23] do not observe any change in isomer shift with 11% substitution of F for O in LaOFeAs. Rotter et al [24] investigated the system Ba$_{1-x}$K$_x$Fe$_2$As$_2$. Their data do not show any significant change in the isomer shift up to 20% substitution of K for Ba. For higher substitutions ranging from 30 to 40%, the data show a decrease in isomer shift, which could also be attributed to structural changes due to monovalent substitution. The question arises as to why Mössbauer studies do not show any change in d-shell population as reflected in the isomer shift. In contrast, there is considerable evidence for a significant increase in electron density in Co- or Ni-doped BaFe$_2$As$_2$ as observed in changes in the Hall coefficient and thermoelectric effect [3, 4, 12–14, 17]. Interestingly, we do observe an additional electron-rich species in single crystals of Ni-doped BaFe$_2$As$_2$ with isomer shift 0.46(1) at 300 K, which is attributed to the fraction of donated electrons residing in the Fe–As channel.

Cobalt and nickel dopants also become a part of the band structure and the additional electron(s) (d$^7$ and d$^8$ versus d$^6$ of Fe(II)) integrate into the system without any change in their formal valence state. In addition, one should take into account two other features. First, the involvement of p orbitals and their hybridization with d orbitals in Fe–As bonding [25] and, second, the contraction of the unit cell resulting in stronger s–p bonding along the As–As channel [26]. These features could provide a conduit for the additional electrons donated by substituents Co or Ni to transfer to the As–As system of itinerant electrons. It would perhaps also lend support to the three-dimensional nature of superconductivity [27].

The proposed model would explain the apparent contradiction between the observation of increased electron density on Co/Ni substitution by changes in the Hall coefficient and thermoelectric effect [3, 4, 12–14, 17], and the absence of an increase in d-shell population as observed by Mössbauer investigations. On the other hand, Wadate et al’s [28] proposal that the extra d electrons donated by Co or Ni are almost totally localized at the substituent site is not in harmony with observations.

### Table 1. Mössbauer spectral parameters—isomer shift (IS, mm s$^{-1}$, ±0.01), quadrupole splitting (QS, mm s$^{-1}$, ±0.01) and hyperfine field (HI, kOe, ±1) for polycrystalline samples prepared at FSU. Observed linewidth 0.29–0.35 mm s$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>300 K IS</th>
<th>300 K QS</th>
<th>78 K IS</th>
<th>78 K QS</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaFe$_2$As$_2$</td>
<td>0.42</td>
<td>0.06</td>
<td>0.53</td>
<td>0.52</td>
</tr>
<tr>
<td>Ba(Fe$<em>{0.6}$Ni$</em>{0.4}$)$_2$As$_2$</td>
<td>0.42</td>
<td>0.10</td>
<td>0.52</td>
<td>0.14</td>
</tr>
<tr>
<td>Ba(Fe$<em>{0.6}$Co$</em>{0.4}$)$_2$As$_2$</td>
<td>0.41</td>
<td>0.13</td>
<td>0.52</td>
<td>0.15</td>
</tr>
<tr>
<td>Ba(Fe$<em>{0.6}$Co$</em>{0.4}$)$_2$As$_2$</td>
<td>0.43</td>
<td>0.01</td>
<td>0.52</td>
<td>0.08</td>
</tr>
<tr>
<td>Ba(Fe$<em>{0.6}$Co$</em>{0.4}$)$_2$As$_2$</td>
<td>0.42</td>
<td>0.05</td>
<td>0.52</td>
<td>0.13</td>
</tr>
</tbody>
</table>

### Acknowledgments

AN, SCB, AK and JGS gratefully acknowledge support from NSF-DMR-MRI 0922735. Work at the NHMFL was supported under NSF Cooperative Agreement DMR-0084173, by the State of Florida and by AFOSR under grant FA 9550-06-1-0474.

### References