

## Magnetization and Electronic Structure of FeAs Layered Material (Pemagnetan dan Struktur Elektronik bagi FeAs Berlapis)

NORIZA AHMAD ZABIDI\*, HASAN ABU KASSIM  
& KESHAV N. SHRIVASTAVA

### ABSTRACT

*Magnetic induction in the superconductor ( $B=H + 4\pi M$ ) in the zero field cooled samples (ZFC) is not equal to zero. Depending upon the chemical environment it has negative value in some and positive values in some others. In the field cooled samples, the magnetization becomes paramagnetic. We have calculated the band structure of one layer of FeAs lattice with spin polarized as well as unpolarized orbitals as a function of doping by Li atoms. For  $n$  number of Li atoms ( $n=0, 1, \dots, 4$ ), we calculated the band gap at all of the  $k$ -points as well as the Fermi energy. The reduced normal state gap was found to lead to superconductivity.*

*Keywords: Band structure; energy gap; FeAs; Fermi energy; magnetic induction*

### ABSTRAK

*Aruhan magnet superkonduktor ( $B=H + 4\pi M$ ) di dalam sampel sejuk bermedan sifar (ZFC) tidak sama dengan sifar. Bergantung kepada persekitaran kimia,  $B$  mempunyai nilai negatif di sesetengah dan nilai positif di sesetengah yang lain. Di dalam sampel sejuk bermedan, pemagnetan menjadi paramagnet. Kami telah mengira struktur jalur satu lapisan kekisi FeAs dengan menggunakan spin terkutub dan juga spin tidak terkutub sebagai suatu fungsi pengedopan oleh atom Li. Untuk bilangan atom Li,  $n$  ( $n=0, 1, \dots, 4$ ), kami telah menghitung jurang jalur pada semua titik- $k$  dan juga tenaga Fermi. Jurang keadaan normal yang berkurangan didapati telah membawa kepada kesuperkonduksian.*

*Kata kunci: Aruhan magnet; jurang tenaga; FeAs; struktur jalur; tenaga Fermi*

### INTRODUCTION

In recent years, Fe containing compounds are found to become superconducting upon doping. FeSe becomes superconducting when the concentration of Se is less than that of Fe at  $T_c = 8.1$  K (Hsu et al. 2008; Mizuguchi et al. 2008). The transition temperature increases up to 18 K in LiFeAs (Tapp et al. 2008). The addition of K atoms leads to an increase up to 38 K (Rotter et al. 2008) and SmFeAsO<sub>1-x</sub>F<sub>x</sub> has a  $T_c$  of 52 K (Jaroszynski et al. 2008; Liu et al. 2008; Zhigadlo et al. 2008). We investigated these materials are interesting from the view point of magnetization and the normal state gap energy. We find that Meissner effect should be modified from zero field to a small finite field. Quantitatively, a small field is present in the Fe containing superconductors. The band structure of FeAs was studied by systematically doping it with Li atoms. Hence, the band gap as a function of number of Li atoms per unit cell was obtained. The normal state gap reduced upon doping in materials which superconduct. In this paper, the modification to the Meissner effect due to a small field and the reduction of normal state gap in FeAs upon doping with Li atoms was studied.

### METHODS

The method of calculation consists of density functional theory electronic program of DMol<sup>3</sup> in the local density

approximation (LDA). The DMol<sup>3</sup> is provided by Accelrys Software Inc. of San Diego, California.

### MAGNETIZATION

The magnetic induction in a material is given by  $B = H + 4\pi M$ , where  $H$  is the external field and  $M$  is the magnetization inside the material. In the Meissner effect,  $B = 0$  so that  $M = \frac{M}{H} = -\frac{1}{4\pi}$ . Since the magnetization is not uniform, the mass density,  $\rho(x)$  depends on the coordinates is introduced. Hence,  $M_0$  is defined as the magnetization per unit mass density so that the volume magnetization becomes  $M = M_0 \rho(x)$ . This leads to the susceptibility,

$$X = \frac{M_0 \rho}{H} \quad (1)$$

with the susceptibility per unit mass density,  $X_0$  so that  $X = X_0 \rho(x)$ . Hence, instead of zero field inside the superconductor, we introduce a small field called  $H_{zero}$  so that,

$$H = \frac{M}{X_0 \rho} \quad (2)$$

The typical susceptibility in some samples of FeSe<sub>0.85</sub> was found to be -0.01055 to -0.0175 emu/g. The mass

density is  $\rho = 5.22 \text{ g/cm}^3$ . Hence the susceptibility  $-0.0155 \times 5.22 = -0.0809 \text{ emu/cm}^3$  is to be compared with  $-1/4\pi = 0.0796$ . Hence, we find from eq. (2) the value of  $H_{\text{zero}} - H$  for this sample to be  $+0.0013$ . In the case of LiFeAs in the zero-field cooled samples  $X(T=0)$  (ZFC) =  $-0.0943$  which is close to ideal diamagnetization ( $4\pi X = -1$ ) (Rotter et al. 2008) and hence  $H_{\text{zero}} - H = +0.0147$ . It is not necessary that  $H_{\text{zero}}$  be positive only. It is possible that the small field inside the superconductor is either parallel or antiparallel to the external field. Hence negative values of  $H_{\text{zero}}$  are also possible. The data is deduced from the work of Tapp et al. (2008). The susceptibility of one sample of LiFeAs which shows the deviation from the  $-1/4\pi$  value in the zero-field cooled LiFeAs, and in the finite field cooled material (Figure 1). A large effect is seen in the finite field cooled samples due to trapped fields.

#### BAND STRUCTURE

A supercell with 4 atoms of Fe and 4 atoms of As was constructed. The unit cell size for this supercell is given by  $a = 7.5828 \text{ \AA}$ ,  $b = 3.7914 \text{ \AA}$  and  $c = 6.3639 \text{ \AA}$ . We optimized the cell for the minimum energy to determine the cell constants. We used the density-functional theory (DFT) to determine the cell constants. We used the density-functional theory (DFT) in the local-density approximation (LDA) to determine the band structure (Kohn & Sham 1965). The coordinates of the k points for which the calculation has been done are, M (0.5, 0.5, 0), A (0.5, 0.5, 0.5), G (0, 0, 0), X (0, 0.5, 0), Z (0, 0, 0.5) and R (0, 0.5, 0.5). We used the spin polarized as well as the spin unpolarized orbitals to calculate the energy. For the FeAs lattice we showed the calculated band structure for the polarized orbitals in Figure 2 and the associated DOS is also included. In the unpolarized, only spin down states are found and the spin up states are completely absent.

Next, we introduced only one Li atom along with 4 atoms of Fe and 4 atoms of As in the supercell and

calculated the band structure as well as the DOS for both the polarized as well as unpolarized orbitals. In this case, it was found that the additional levels were introduced in between M and A points, so that the gap is reduced and structure appears in the DOS. The gap of the normal state reduced upon doping with Li. This result was obtained by our DFT calculation. Quite apart from this result, the experimental information is that  $T_c$  of the superconductor increases upon doping with Li or oxygen. If we combine our calculated result with the experimental result, we find that reduced normal state gap is accompanied with increased critical temperature. Hence, we find that the reduced normal state gap leads to superconductivity. The band structure of 4 Fe 4 As 1 Li is shown in Figure 3. A comparison of band structure of 4 Fe 4 As with that of 4 Fe 4 As 1 Li shows that the DOS is also increased upon doping with Li. Similarly, we calculated the band structure of FeAs by doping the cell with 2, 3 and 4 Li atoms. In going from 0 to 1 Li atom the gap at M point reduces from 1.1 to 0.50 eV. The gap further reduces to 0.47 eV when 2 Li atoms are introduced. The gap is 0.04 eV for 3 Li atoms but it increased to 0.70 eV for 4 Li atoms. Therefore, small amount of Li doping reduces the gap but large amount of Li increases it. At A point, the gap continuously reduced upon increasing the number of Li atoms from 0 to 4. At the G point the gap reduced upon introducing the Li atoms except for 3 Li atoms where it increased.

The energy is given in Table 1. The Fermi energy and the binding energy calculated from DFT (LDA) as a function of number of Li atoms is given in Table 2. The Fermi energy reduces when one Li atom is added to FeAs zig-zag layer but it increases as the number of Li atoms is increased. The small decrease in the Fermi energy helps in forming a superconducting state but the same can not be done by adding excessive amount of Li atoms. The binding energy has a peak when three atoms of Li are added to FeAs.

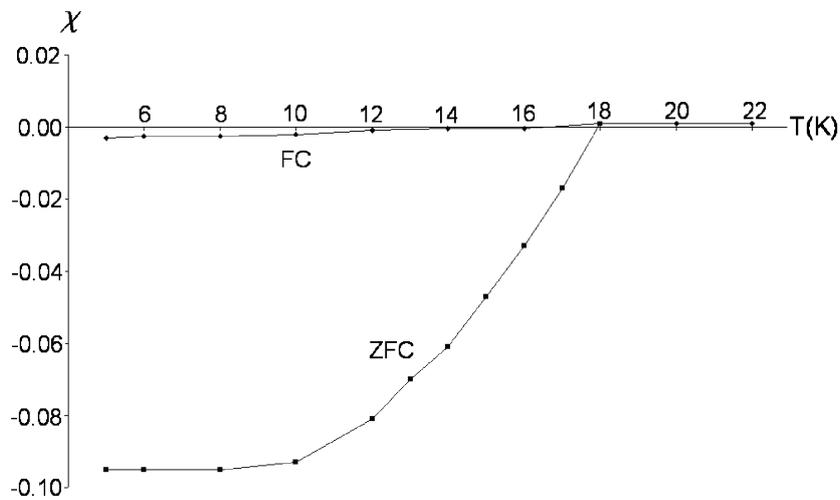


FIGURE 1. The susceptibility of LiFeAs showing deviation from  $-1/4\pi$  value

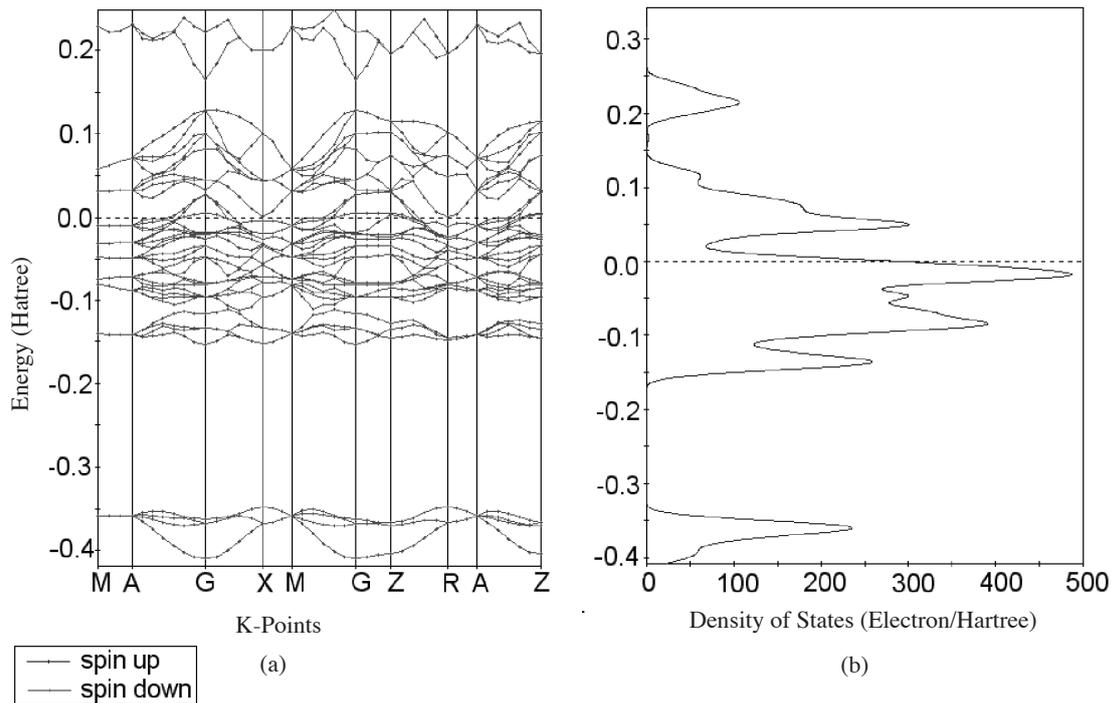


FIGURE 2. (a) The band structure of FeAs and (b) the DOS calculated from first principles by using DFT (LDA)

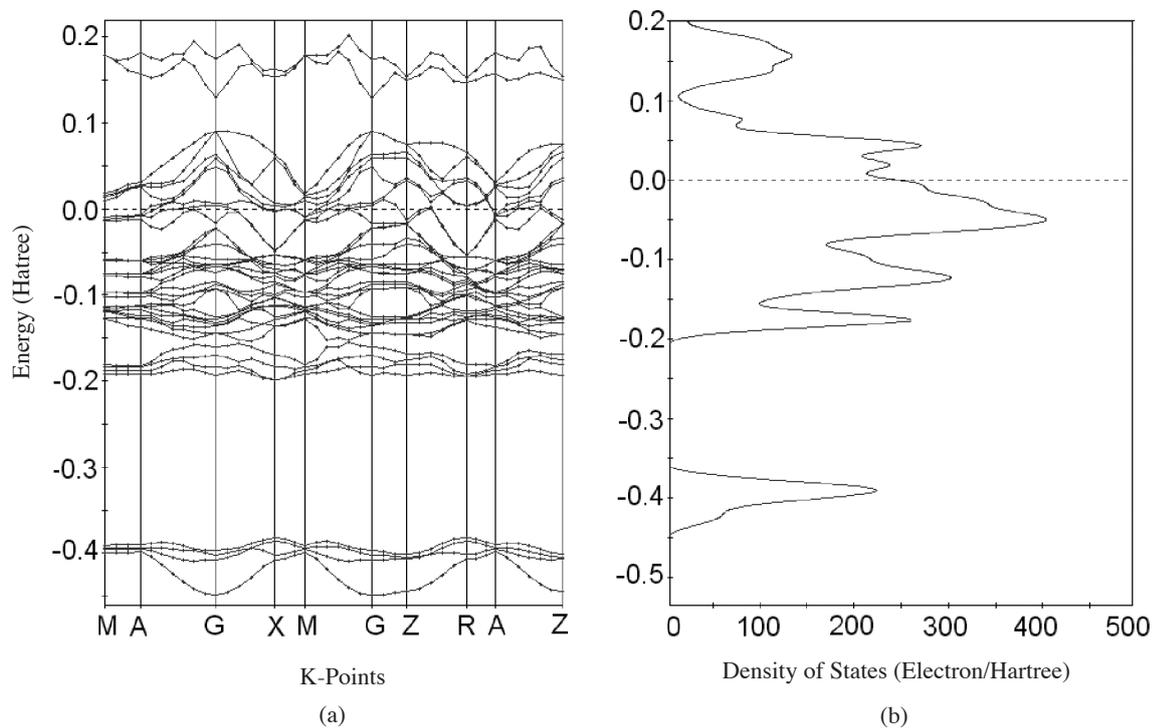


FIGURE 3. (a) The band structure of LiFeAs and (b) the DOS showing the effect of doping with Li atoms

#### CONCLUSION

We find that in the Meissner effect, the field inside a superconductor should be zero but this statement requires modification. There may be a small field inside the material due to field trapping at the Fe site. In FeAs superconductors,

there is a small field even in the superconducting state. The magnetization of these materials depends on the coordinates so that uniform susceptibility is modified. The band gap of FeAs reduced upon adding Li. This reduced normal state gap is conducive to a superconducting state.

TABLE 1. The gap energies of LiFeAs with various k-points using spin unpolarized calculation

	4 atoms Lithium (eV)	3 atoms Lithium (eV)	2 atoms Lithium (eV)	1 atoms Lithium (eV)	No atoms Lithium (eV)
M	0.7007	0.6395	0.7891	0.5034	1.1021
A	0.6327	0.6531	0.7973	0.898	1.1837
G	0.1905	0.3265	0.7211	0.5578	0.6395
X	0.4626	0.6123	0.5306	0.1633	0.1497
M	0.7007	0.6395	0.7891	0.5034	1.1021
G	0.1905	0.3265	0.7211	0.5578	0.6395
Z	0.3402	0.4762	0.1157	1.2245	0.6531
R	1.1701	0.7687	0.6803	1.5375	0.3402
A	0.6327	0.6531	0.7973	0.898	1.1837
Z	0.3402	0.4762	0.1157	1.2245	0.6395

TABLE 2. The Fermi energy and the binding energy calculated from spin unpolarized orbital

	4 atoms Lithium (eV)	3 atoms Lithium (eV)	2 atoms Lithium (eV)	1 atoms Lithium (eV)	No atoms Lithium (eV)
Fermi energy	6.8772	6.7839	6.7749	6.3106	6.3785
Binding energy	55.7756	51.8866	48.4033	123.7746	41.7099

In previous studies, we have found that the calculation of band structure in solids gives useful information related to the solid state properties of materials (Zabidi et al. 2009a, 2009b, 2009c).

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Department of Physics  
Faculty of Science  
University of Malaya  
50603 Kuala Lumpur  
Malaysia

\*Corresponding author; email: nazca\_leo@hotmail.com

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