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Frustrated magnetic interactions, giant magneto–elastic coupling, and magnetic phonons in iron–pnictides

Taner Yildirim *

NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA

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ABSTRACT

We present a detailed first-principles study of Fe-pnictides with particular emphasis on competing magnetic interactions, structural phase transition, giant magneto–elastic coupling and its effect on phonons. The exchange interactions $J_{i,j}(R)$ are calculated up to ≈12 Å from two different approaches based on direct spin-flip and infinitesimal spin-rotation. We find that $J_{i,j}(R)$ has an oscillatory character with an envelop decaying as $1/R^3$ along the stripe-direction while it is very short range along the diagonal direction and antiferromagnetic. A brief discussion of the neutron scattering determination of these exchange constants from a single crystal sample with orthorhombic-twinning is given. The lattice parameter dependence of the exchange constants, $dJ_{i,j}/da$ are calculated for a simple spin-Peierls like model to explain the fine details of the tetragonal–orthorhombic phase transition. We then discuss giant magneto–elastic effects in these systems. We show that when the Fe-spin is turned off the optimized *c*-values are shorter than experimental values by 1.4 Å for $CaFe_2As_2$, by 0.4 Å for $BaFe_2As_2$, and by 0.13 Å for LaOFeAs. We explain this strange behavior by unraveling surprisingly strong interactions between arsenic ions, the strength of which is controlled by the Fe-spin state through Fe–As hybridization. Reducing the Fe-magnetic moment, weakens the Fe–As bonding, and in turn, increases As–As interactions, causing a giant reduction in the *c*-axis. These findings also explain why the Fe-moment is so tightly coupled to the As-z position. Finally, we show that Fe-spin is also required to obtain the right phonon energies, in particular As c-polarized and Fe–Fe in-plane modes that have been recently observed by inelastic X-ray and neutron scattering but cannot be explained based on non-magnetic phonon calculations. Since treating iron as magnetic ion always gives much better results than non-magnetic ones and since there is no large *c*-axis reduction during the normal to superconducting phase transition, the iron magnetic moment should be present in Fe-pnictides at all times. We discuss the implications of our results on the mechanism of superconductivity in these fascinating Fe-pnictide systems.

1. Introduction

The recent discovery of superconductivity at T_c's up to 55 K in iron–pnictide systems [1–4] has sparked enormous interest in this class of materials. So far four types of materials have been discovered. The first one is the rare-earth pnictide oxide layered systems, REOFeAs which is denoted as "1111" [1–5]. The second class is the so called "122" systems with the chemical formula MFe_2As_2 (M = Ca,Sr, etc.) [9,6–8,5]. The third system with T_c = 18 K is MFeAs (M = Li and Na), which is similar to REOFeAs but instead of REO-layers, we have now small alkali metals such as Li [10]. The last one is the binary Fe(Se,Te) systems which have been shown to superconduct up to 12 K under pressure [11].

The crystal structures of these four systems are shown in Fig. 1. The common feature in these Fe-pnictide superconductors is the presence of FeAs plane (or Fe(Te,Se) in the case of 11 systems), which is shown in Fig. 2. Basically Fe-atoms form a regular square lattice just like the CuO_2 plane in cuprates. However the important difference is the location of the arsenic ions which are not located between two Fe ions but rather above/below the center of Fe-square. This arrangement of arsenic ions has several important consequences in the electronic and magnetic properties of these systems. Since As is not directly between two Fe ions, the Fe–Fe distance is not large and direct Fe–Fe overlap plays an important role in the band formation near the Fermi level. Then, the delicate interplay between Fe–Fe, Fe–As, and even As–As interactions (which is very important in 122 systems such as Ca122) result interesting electronic and magnetic properties that are super-sensitive to the As-*z* position and the *c*-lattice parameter of the Fe-pnictide system. In this paper, we will focus on the structural,

* Address: NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.
E-mail address: taner@nist.gov

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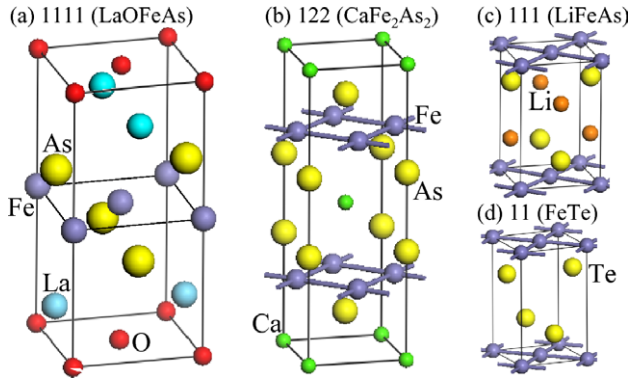

Fig. 1. The crystal structures (with origin choice one) of four types of Fe-pnictide systems that have been discovered so far.

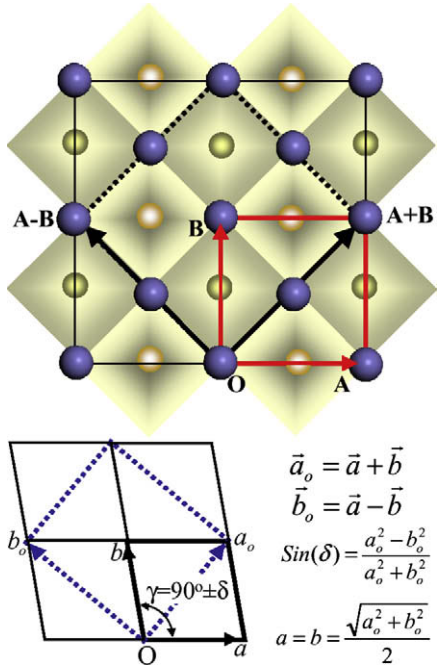

Fig. 2. Top: A view along *c*-axis of the FeAs-plane and the relations between the primitive and $\sqrt{2} \times \sqrt{2}$ supercell used in our calculations. The dark and light shaded areas indicate the As-atoms below and above the Fe-square lattice, respectively. Bottom: Relation between conventional (Cmma) and primitive (P2/*c*) cells of the orthorhombic structure.

dynamical and magnetic properties of 1111 and 122 systems only. For a recent review of electronic and superconducting properties of Fe-based superconductors, we refer the reader to David Singh's [12] and Igor Mazin's [13] articles in this issue and references therein.

A common phase diagram for iron–pnictides has emerged [14] in which the stoichiometric parent compound shows a structural anomaly around 150–200 K, below which spin-density-wave (SDW) antiferromagnetic ordering [15,16,6–8] appears, which is due to nesting Fermi-surfaces [18–20,17]. The SDW ordering is further stabilized against the normal checkerboard antiferromagnetic ordering (denoted as AF1) due to strong antiferromagnetic interactions along the Fe-square-diagonal [21]. Superconductivity in these systems only occurs when the SDW ordering and the structural distortion are suppressed, which can be achieved in a number of ways such as fluorine doping on the oxygen site [1–4], or hole doping ($La_{1-x}Sr_x$) [23–25,22] or by applying external pressure [26–28].

The structural distortion which is common to all parent compounds can be characterized by either primitive monoclinic space group P2/*c* (P112/*n*) or the conventional orthorhombic cell with space group Cmma [29]. The relation of these two representations is indicated in the bottom panel of Fig. 2. We note that when the system is distorted (i.e. $\gamma \neq 90.0$) one of the Fe-pairs gets closer and the other Fe–Fe distance gets longer, yielding an orthorhombic lattice (i.e. $a_o \neq b_o$). Below we will successfully explain how this structural phase transition is tightly coupled to the magnetic SDW ordering. Finally we note that the reported space groups in the SDW state [15,29] (i.e. Cmma or P2/*c*) are actually the space groups of the system without the Fe-magnetic moment. Hence technically the Cmma is not the right space group for the SDW magnetic system. If we ignore the antiferromagnetic stacking of the FeAs planes, the actual space group is Pbnm which is primitive as expected. This will be important in the discussion of magnetic phonon calculations in Section 6 where we can not use the space group Cmma but has to use Pbmb for 1111 systems. The situation is very similar for the 122, 111, and 11 systems as well. For example, the Fmmm space group of 111 systems is actually reduced to Bbmb (spg. number = 66, origin 1) when the iron-spins are considered.

Clearly, the understanding of electronic, magnetic, and structural properties of the parent FeAs compound is the key to determining the underlying mechanism that makes these materials superconduct upon electron/hole doping. In this paper we present a detailed first-principles study of Fe-pnictides with main focus on the competing magnetic spin-interactions, structural phase transition, the giant magneto–elastic coupling and the phonons. Our main objective is to demonstrate that Fe-spin is the key in understanding many properties of these systems, including lattice parameters, atomic positions, and the phonon spectrum. When the Fe-spin is ignored and non-magnetic calculations are done, the results do not agree with most of the experimental data. This observation could be the key in identifying the mechanism of superconductivity in these systems.

This paper is organized as follows. In the next section, we discuss the energetics of possible spin-configurations in Fe-pnictides within a unified model from all-electron fix-spin-moment calculations. We will show that the SDW magnetic ordering is the only stable ground state for Fe-pnictide. In Section 3, we will calculate the exchange interactions $J_{i,j}(R)$ up to ≈12 Å using two different approaches based on direct spin-flip and infinitesimal spin-rotation. We find that $J_{i,j}(R)$ has an oscillatory character with an envelop decaying as $1/R^3$ along the stripe-directions. On the other hand, it is short range along the diagonal direction and antiferromagnetic, suggesting it is superexchange type and an important contributor towards the stabilization of SDW ordering. A brief discussion of the experimental determination of these exchange constants from an orthorhombic-twin crystal is also given in this section. In Section 4, we will discuss the tetragonal–orthorhombic lattice distortion. We will calculate the lattice parameter dependence of the exchange constants, $dJ_{i,j}/da$, and then use it in a simple spin-Peierls like model to explain the fine details of the tetragonal–orthorhombic phase transition that is driven by the SDW ordering. In Section 5, we will discuss the giant magneto–elastic effects in these systems where iron-spin controls the strength of Fe–As and As–As hybridization which results huge dependence of the magnetic and structural properties on the As-z and *c*-axis of the lattice. Finally, in Section 6, we show that Fe-spin is also required to obtain the right phonon energies, in particular As c-polarized and Fe–Fe in-plane modes that have been recently observed by inelastic X-ray and neutron scattering measurements but could not been explained based on non-magnetic phonon calculations. Our conclusions will be given in Section 7.