Spin-Peierls-like transition in AFe$_2$As$_2$ (A=Ba, Sr)

D. Hou,$^{1,2}$ Q. M. Zhang,$^1$ Z. Y. Lu,$^1$ and J. H. Wei$^1$

$^1$Department of Physics, Renmin University of China, Beijing 100872, P. R. China
$^2$School of Physics, Shandong University, Jinan 250100, P. R. China

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From first-principles density functional theory calculations combined with varying temperature Raman experiments, we show that AFe$_2$As$_2$ (A=Ba, Sr), the parent compound of the FeAs based superconductors of the new structural family, undergoes a spin-Peierls-like phase transition at low temperature. The coupling between the phonons and frustrated spins is proved to be the main cause of the structural transition from the tetragonal to orthorhombic phase. These results well explain the magnetic and structural phase transitions in AFe$_2$As$_2$(A=Ba, Sr) recently observed by neutron scattering.

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Introduction

The recent discovery of iron-based high-transition temperature (high-$T_c$) superconductors$^1$ has invoked great research interests in similar materials with Fe-As layers. Currently, the focuses are mainly on two kinds of structures: the first is iron arsenide-oxides with P4/nmm space group$^{2,3,4}$, represented by the parent compound LaFeAsO, and the second is ternary iron-arsenic compound with body-centered I4/mmm space group$^{5,6,7}$, represented by the parent compound BaFe$_2$As$_2$$^8$. Those compounds show similar structural and magnetic properties. At room temperature, they all lay in non-magnetic, high-symmetric state, with Fe-As layers separated by La-O layers or Ba layers respectively. With the decrease of temperature, LaFeAsO undergoes a slight structural transition from the tetragonal to orthorhombic phase at $T_a=150$K, followed by the appearance of a magnetic SDW (spin-density wave) state at 134K$^8$, while BaFe$_2$As$_2$ experiences a similar structural and magnetic transition simultaneously at about $T_a=140$K$^9$. At the magnetic SDW state, they all form a collinear stripe-ordering magnetic ground-state, with the nearest Fe atoms aligning anti-ferromagnetically along one crystal axis in Fe-As plane, while ferromagnetically parallel to the other axis$^8$$^2$$^3$$^{10}$$^{11}$. By doping with electron or hole carriers, the structure transition and the SDW state are both suppressed, and the superconductivity emerges at 52K$^{12}$ and 38K$^{13}$ respectively. Thus there exists a competition between magnetism and superconductivity in these compounds, but the subtle details such as the pairing mechanism are far from clear.

As that in high-$T_c$ cuprates, revealing the mechanism of superconductivity of iron-based superconductors highly requires understanding the electronic, structural and magnetic properties of parent compounds first. The structural and magnetic phase transitions seem to be common features in these Fe-As based superconductors, thus revealing the sources of these transitions and the possible connections between them may lead to better understandings of the experimental observations. Some first-principles density functional theory (DFT) calculations have suggested that the frustrated superexchange interactions between Fe ions induces the collinear stripe antiferromagnetic ground state$^{10}$, on the other hand the main cause of the structural phase transition, as well as its correlation to the magnetic one, is not well understood so far.

Let us start with the frustrated $J_1−J_2$ Heisenberg model to describe the nearest neighbor and next-nearest neighbor superexchange interactions among the Fe atoms bridged by As atoms, which can be described as$^{10}$

$$H = J_1 \sum_{<ij>} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j, \quad (1)$$

where $<ij>$ and $\langle ij \rangle$ denote the summation over the nearest and the next-nearest neighbors respectively. The ground state of the frustrated $J_1−J_2$ spin-half model on a square lattice at zero temperature has been studied by several groups in the literature and the main results are summarized as follows$^{12}$$^{16}$:

1. In the absence of frustration ($J_2=0$), its ground state has long-range Néel order; (2) With the increase of frustration ($J_2/J_1$), a phase transition from Néel order to a spin-liquid phase occurs; (3) If further increasing the frustration, a collinear order emerges at $J_2/J_1 \gtrsim 0.55$, with the nearest spins aligning anti-ferromagnetically along one axis while ferromagnetically parallel to the other.

According to the DFT calculation in Ref.$^{10}$, $J_1$ almost equals to $J_2$ for Fe-As superconductors. In this sense, the DFT and model calculations consistently explain the collinear magnetic order of the parent compounds. However, the ground state given by $J_1−J_2$ model is twofold degenerate with the $\pi/2$ rotational symmetry, which is not in agreement with the orthorhombic structure observed in experiments. It indicates that the pure spin model is not sufficient to account for the structural phase transition. We hereby suggest to extend $J_1−J_2$ model by evolving the spin-phonon coupling. For examples, when adiabatic phonons are considered, the model should be
modified as,

\[ H = \sum_{<ij>} [J_1(1 - \alpha_1 y_{ij})\vec{S}_i \cdot \vec{S}_j + \frac{K_1}{2} y_{ij}^2] + \sum_{<<ij>} [J_2(1 - \alpha_2 y_{ij})\vec{S}_i \cdot \vec{S}_j + \frac{K_2}{2} y_{ij}^2] \tag{2} \]

where \( y_{ij} = |\vec{u}_j - \vec{u}_i| \) with \( \vec{u}_i \) denoting the in-plane displacement of atom \( i \), \( \alpha \) is the spin-phonon coupling constant. The ground state (at \( T = 0 \)) of above model was calculated with a spin-wave approximation in recent literature and a Peierls-like transition from a tetragonal to an orthorhombic phase was found at large frustration \((J_2/J_1 \gtrsim 0.5)\)\(^{(17)}\).

In this letter, motivated by the model analysis, we use the first-principles density functional calculations combined with varying temperature Raman experiments to study the ground state of \( \text{AFe}_2\text{As}_2 \) (A=Ba, Sr). We prove that the spin-Peierls-like phase transition is the very mechanism of the structural transition at \( T_a \) in the parent compounds of iron-based superconductors.

Method The calculation was done using a plane-wave based method\(^{(18)}\) with local spin density approximation (LSDA) and generalized gradient approximation (GGA) of Perdew-Burke-Ernzerh (PBE)\(^{(19)}\) for the exchange-correlation potentials. The density-functional perturbation theory (DFPT) was used to calculate the \( \Gamma \)-point phonons. Firstly, the electronic properties of \( \text{AFe}_2\text{As}_2 \) (A=Ba,Sr) were calculated to determine the electronic ground state, using experimental cell parameters\(^{(6)}\) and energy-minimized internal atomic positions. Different magnetic configurations, namely the nonmagnetic, square anti-ferromagnetic and collinear anti-ferromagnetic were considered\(^{(10)}\). The ground states of both \( \text{BaFe}_2\text{As}_2 \) and \( \text{SrFe}_2\text{As}_2 \) are found to be collinear anti-ferromagnetic with a slight structure transition, which is in agreement with previously reported results. For the phonon calculations, we focus on the nonmagnetic high-temperature state and the collinear anti-ferromagnetic ground state at low temperature. Here we adopt the triclinic primitive unit cells as shown in Fig. 1, in which the structure transition alters the angle between \( x \) and \( y \) crystal axes from 90° to 89.6°.

The Raman measurements were performed with a triple-grating monochromator (Jobin Yvon T64000), which works with a microscopic Raman configuration. A 50× objective microscopic lens with a working distance of 10.6 mm, is used to focus the incident light on sample and collect the scattered light from sample. The detector is a back-illuminated CCD cooled by liquid nitrogen. An solid-state laser (Laser Quantum Torus 532) with high-stability and very narrow width of laser line, is used with an excitation wavelength of 532 nm. The laser beam of 3 mW was focused into a spot of less than 10 microns in diameter on sample surface.

Result From symmetry analysis, the Raman phonon of nonmagnetic \( \text{AFe}_2\text{As}_2 \) with \( 14/mmm \) space group consists of four modes: the \( A_{1g} \) and \( E_g \) for As, the \( B_{1g} \) and \( E_g \) for Fe. The vibrating directions in \( A_{1g} \) and \( B_{1g} \) modes are perpendicular to the Fe-As layer, while that of \( E_g \) parallel to the Fe-As layer. After cooling down to the transition temperature \( T_a \), the crystal structure changes into orthorhombic \( F/mmm \) space group, and the magnetism appears almost at the same temperature. In this space group, the \( E_g \) modes split into \( B_{2g} \) and \( B_{3g} \) modes, and \( A_{1g} \) mode for As changes into \( B_{2g} \) mode. The calculated Raman modes, as listed in Table 1, are in good agreement with symmetry analysis. All of the modes have been found and assigned from atomic displacements.

The Raman modes of \( \text{SrFe}_2\text{As}_2 \) have been measured in Ref.\(^{(20)}\) but only for nonmagnetic state reported. By comparing our calculated phonon frequencies with the experimental values, we find a systematic frequency shift (\( \sim 20 \text{cm}^{-1} \)) of the calculated values towards higher value region (see Table 1) due to the temperature effect. That is to say, the DFPT theory deals with the ground-state problems, which in this case corresponds to a non-magnetic state at \( T = 0 \text{K} \), while the Raman spectra was measured at room temperature, as a consequence, the corresponding experimental values are lower.

Since the strong spin-phonon interaction is the basis of the suggested mechanism of spin-Peierls-like phase transition, we must verify this point first, by calculating the change of the Raman modes in nonmagnetic state without the magnetic transition but with the structural transition. In that case, the calculated Raman modes and frequencies almost remain unchanged for both \( \text{BaFe}_2\text{As}_2 \) and \( \text{SrFe}_2\text{As}_2 \), with frequency shifts (or splits) less than 3 \text{cm}^{-1}. This suggests that the slight structure transition has limited effects on the electronic properties and Raman phonons. Our tentative calculations also gives us another valuable information: the \( E_g \) mode of Fe atom experiences a frequency splitting as a result of the structural transition, which consists with the fact that the structure distortion mainly appears in Fe-As layer and changes the nearest neighbor Fe-Fe distances slightly, so that the nearest neighbor Fe-Fe distances are no longer

\[ 3 \text{mW} \]

3 cm

10 microns

532 nm

3 mW

90°

89.6°

\( \alpha \)

\( \vec{u}_i \)

\( y_{ij} \)

\( |\vec{u}_j - \vec{u}_i| \)

\( \alpha \)

\( \vec{S}_i \cdot \vec{S}_j \)

\( \sum_{<ij>} \)

\( \sum_{<<ij>} \)

\( J_1 \)

\( \alpha_1 \)

\( y_{ij} \)

\( \frac{K_1}{2} \)

\( J_2 \)

\( \alpha_2 \)

\( y_{ij} \)

\( \frac{K_2}{2} \)

\( \Gamma \)

\( \vec{S}_i \cdot \vec{S}_j \)

\( \sum_{<ij>} \)

\( \sum_{<<ij>} \)

\( J_1 \)

\( \alpha_1 \)

\( y_{ij} \)

\( \frac{K_1}{2} \)

\( J_2 \)

\( \alpha_2 \)

\( y_{ij} \)

\( \frac{K_2}{2} \)

\( \Gamma \)

\( \vec{S}_i \cdot \vec{S}_j \)

\( \sum_{<ij>} \)

\( \sum_{<<ij>} \)

\( J_1 \)

\( \alpha_1 \)

\( y_{ij} \)

\( \frac{K_1}{2} \)

\( J_2 \)

\( \alpha_2 \)

\( y_{ij} \)

\( \frac{K_2}{2} \)

\( \Gamma \)

\( \vec{S}_i \cdot \vec{S}_j \)

\( \sum_{<ij>} \)

\( \sum_{<<ij>} \)

\( J_1 \)

\( \alpha_1 \)

\( y_{ij} \)

\( \frac{K_1}{2} \)

\( J_2 \)

\( \alpha_2 \)

\( y_{ij} \)

\( \frac{K_2}{2} \)

\( \Gamma \)

\( \vec{S}_i \cdot \vec{S}_j \)

\( \sum_{<ij>} \)

\( \sum_{<<ij>} \)

\( J_1 \)

\( \alpha_1 \)

\( y_{ij} \)

\( \frac{K_1}{2} \)

\( J_2 \)
equal in the orthorhombic crystal axes directions.

Table 1: Raman phonon frequencies of AF2As2(A=Ba,Sr) in the non-magnetic state (marked as N) and in the collinear anti-ferromagnetic state (marked as C). The Raman modes are in I4/mmm space group corresponding to the non-magnetic state, while those in the brackets are in P/mmm space group for the collinear anti-ferromagnetic state. The measurement temperatures are 260K and 87K for SrFe2As2, and 290K and 100K for BaFe2As2. The atomic displacements are for the collinear anti-ferromagnetic state.

| Atom | Raman Mode | SrFe2As2-N | SrFe2As2-C | BaFe2As2-N | BaFe2As2-C | Displacement of Atoms, C |
|------|------------|------------|------------|------------|------------|-------------------------|
| As   | E_g(B_2g)  | 138.9      | 96.1       | 140.2      | 86.8       | As(x), Fe(y)             |
| As   | E_g(B_3g)  | 138.9      | 126.3      | 140.2      | 125.6      | As(y), Fe(x)             |
| As   | A_1g(B_g)  | 207.6      | 183.4      | 205.7      | 177.8      | As(z)                   |
| Fe   | B_1g(B_1g) | 219.5(206)| 219.3(213)| 224.0(206)| 214.2(212)| Fe(z)                   |
| Fe   | E_g(B_2g)  | 301.2      | 262.4      | 293.6      | 252.0      | Fe(y), As(x)             |
| Fe   | E_g(B_3g)  | 301.2      | 289.0      | 293.6      | 281.1      | Fe(x), As(y)             |

We are now on the position to elucidate the changes of the Raman modes due to spin-phonon interactions at the magnetic ground state. Our calculations on the electronic structure verify that the magnetic ground state of AF2As2(A=Ba, Sr) is a collinear stripe-ordering anti-ferromagnetic one. The Fe spins align parallel along the shorter axis in Fe-As layer and anti-parallel along the longer one, as observed by neutron diffraction measurement[9], which is similar to that of LaFeAsO[8]. To correctly illustrate this magnetic configuration, the nonmagnetic primitive unit cell should be doubled in a-b plane to include two formula cells. Here we adopt a \( \sqrt{2} \times \sqrt{2} \times 1 \) cell, with x(y) axis rotates 45° and points to the nearest Fe-Fe directions. By doubling the crystal lattice, the reciprocal lattice rotates and shrinks to a half, and the original reciprocal points fold down to the new points. The folding is illustrated in Fig. 2 (the structure distortion from tetragonal to orthorhombic not shown in the figure). It is clear that original M(\( \pi, \pi, 0 \)) points fold down to the new \( \Gamma(0, 0, 0) \) point. Thus the obtained \( \Gamma \) point phonon modes in SDW state doubly contain the information from both original \( \Gamma \) and M points. Only the modes corresponding to \( \Gamma \) point are picked up according to the atomic displacements, which are shown in Table 1 (marked as C). For the purpose of comparison, we also show the measured Raman phonons at different temperatures before and after the magnetic transitions in the table. The calculated phonon frequencies are found very close to the experimental values, which further proves the reliance of our phonon calculations.

As shown in Table 1, accompanied with the onset of magnetism, almost all of the Raman phonon frequencies softened to lower values, specifically some of them (As-B_2g and Fe-B_2g) show a giant phonon softening (GPS). The GPS of Raman phonon modes is the main result of our DFT calculations, which directly support the mechanism of the spin-Peierls-like phase transition at \( T_a \) in AFe2As2(A=Ba, Sr). Let us elaborate this point in more details as follows:

Firstly, by comparing the changes of B_3g and B_2g frequencies of Fe atoms (seen in Table 1), one can see that the former only reduces 12cm\(^{-1}\) for both BaFe2As2 and SrFe2As2 while the latter reduces 41cm\(^{-1}\) for BaFe2As2 and 39cm\(^{-1}\) for SrFe2As2 (GPS). The difference between these two modes is the involved Fe atoms vibrating in different direction - along x and y crystal axis respec-
tively. In SDW state, the spins on Fe atoms align antiparallel along x (longer) direction, while parallel along y (shorter) direction. In B2g mode, the vibration direction of Fe atoms accords with the parallel spin direction, suggesting an instability of parallel alignment of Fe spins.

Secondly, if assuming \( \gamma^{x,y}_{\langle ij \rangle} = \delta^{x,y}, \gamma^{x,y}_{\langle ij \rangle} = \delta^{z} + \delta^{y} \), \( \alpha_1 = \alpha_2 = \alpha \) and \( K_1 = K_2 = K \) in the extend \( J_1 - J_2 \) model [see Eq. (2)], one can obtain the collinear state (ground state) with \( \delta^{x} = \alpha(J_2 - J_1)/4K \) and \( \delta^{y} = \alpha(J_2 + J_1)/4K \) at sufficient large frustration \( J_2/J_1 > 0.5 \). In consideration of \( J_2 \sim J_1 \) in AF \( \text{Fe}_2\text{As}_2 \), one can reach \( \delta^{y} \gg \delta^{x} \), which consistently explains why the GPS of Raman modes of Fe atoms mainly happens along y crystal axis.

Thirdly, the spin-Peierls-like phase transition proved by the DFT and model analysis here closely relates to the "exchange striction" effect that also predicts symmetry breaking distortions from the magnetoelastic to the "exchange striction" effect that also predicts by the DFT and model analysis here closely relates crystal axis.

Summary In summary, the consistence of the first-principles density functional calculations and model analysis strongly prove that the spin-Peierls-like phase transition is the very mechanism of the structural transition at \( T_c \) in parent compounds of iron-based superconductors. We thus conclude that the dominate interactions in those parent compounds are frustrated spin-spin interaction and spin-phonon interaction. Electron or hole doping suppresses the ground state of parent compounds (orthorhombic structural and collinear magnetic phase) and induces the superconductor state. In order to understand the pairing mechanism for ion-based new superconductors, one should treat the spin-spin and spin-phonon interactions on an equal footing.

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* Electronic address: wjh@ruc.edu.cn

[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
[2] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen and D. F. Fang, Nature 453, 761-762 (2008).
[3] G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, Phys. Rev. Lett. 100, 247002 (2008).
[4] Zhi-An Ren, Jie Yang, Wei Lu, Wei Yi, Guang-Can Che, Xiao-Li Dong, Li-Ling Sun, Zhong-Xian Zhao, Materials Research Innovations 2008 VOL 12 NO 3, 1.
[5] M. Rotter, M. Tegel, I. Schellenberg, W. Hermes, R. Pöttgen, and D. Johrendt, Phys. Rev. B 78, 020503(R) (2008).
[6] C. Krellner, N. Caro-ca-anales, A. Jesche, H. Rosner, A. Ormeci, and C. Geibel, Phys. Rev. B 78, 100504(R) (2008).
[7] G. F. Chen, Z. Li, G. Li, W. Z. Hu, J. Dong, X. D. Zhang, P. Zheng, N. L. Wang, and J. L. Luo, Chin. Phys. Lett. 25, 3403 (2008).
[8] Clarina de la Cruz, Q. Huang, J. W. Lynn, Jiying Li, W. Ratcliff II, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, Pengcheng Dai, Nature 453, 899-902 (2008).
[9] Q. Huang, Y. Qiu, Wei Bao, J.W. Lynn, M.A. Green, Y.C. Gasparovic, T. Wu, G. Wu, and X. H. Chen, Phys. Rev. Lett. 101, 257003 (2008).
[10] Fengjie Ma, Zhong-Yi Lu and Tao Xiang, arXiv:0806.3526.
[11] J. Dong, H. J. Zhang, G. Xu, Z. Li, G. Li, W. Z. Hu, D. Wu, G. F. Chen, X. Dai, J. L. Luo, Z. Fang, and N. L. Wang, Europhysics Letters, 83, 27006 (2008).
[12] Zhi-An Ren, Jie Yang, Wei Lu, Wei Yi, Xiao-Li Shen, Zheng-Cai Li, Guang-Can Che, Xiao-Li Dong, Li-Ling Sun, Fang Zhou, Zhong-Xian Zhao Europhysics Letters, 82 (2008) 57002.
[13] M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. 101, 107006 (2008).
[14] Y. Yildirim, Phys. Rev. Lett. 101, 057010 (2008).
[15] P. Chandra and B. Doucot, Phys. Rev. B 38, 9335 (1988).
[16] P. Chandra, P. Coleman and A. I. Larkin, Phys. Rev. Lett. 64, 88 (1990).
[17] F. Becca and F. Mila, Phys. Rev. Lett. 89, 037204 (2002).
[18] P. Giannozzi et al., http://www.quantum-espresso.org.
[19] J. P. Perdew, K. Burke, and M. Erznerhof, Phys. Rev. Lett. 77, 3865 (1996).
[20] A. P. Litvinchuk, V.G. hadjiiev, M.N. Iliev, B. Lv, A.M. Guloy, and C.W. Chu, Phys. Rev. B 78, 060503(R) (2008).
[21] J. B. Goodenough, Magnetism and the Chemical Bond (InterScience and John Wiley, New York, 1963).