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# Magnetoelastic Coupling, Negative Thermal Expansion, and Two-dimensional Magnetic Excitations in FeAs

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## Abstract

We present a temperature-dependent investigation of the local structure and magnetic dynamics of the FeAs binary. The magnetic susceptibility  $\chi(T)$  result shows an anomalous broad feature up to 550 K, with  $\chi$  continuing to increase above the Néel antiferromagnetic ordering temperature ( $T_N = 70$  K), peaking at  $\sim 250$  K, then decreasing gently above. It is remarkable that this peak susceptibility temperature corresponds to the onset of anisotropic negative thermal expansion (NTE) in both the  $a$  and  $c$ -axes, suggesting that magnetic interactions are affecting the structure even well above the Néel point. A systematic investigation into local bonding correlations, from time-of-flight neutron pair distribution function (PDF) analyses, shows the octahedral volume around each Fe site growing monotonically while adjacent octahedra tilt toward one another before relaxing away past this peak in the anomalous magnetic susceptibility. We use inelastic-neutron scattering to map spin-wave excitations in FeAs at temperatures above and below the  $T_N$ . We find magnetic excitations near  $T_N$  to be very different from the excitations in the ground state at 1.5 K. Spin-waves measured at 1.5 K are three dimensional (3D), however, in vicinity of the magnetic transition, the magnetic fluctuations clearly indicate two-dimensional (2D) character in this intrinsically 3D crystal structure. Unlike the undoped 2D parents of iron-arsenide superconductors, where the magnetic correlations are considerably weaker along the  $c$ -axis than in the  $ab$ -plane, inelastic neutron scattering here shows that the spin fluctuations in the 3D FeAs binary are nearly 2D in the  $bc$ -plane at 90 K. These results demonstrate the importance of short-range correlations in understanding the magnetic properties of transition-metal binaries, and suggest how 2D excitations, even in a 3D structure, can potentially become a breeding ground for unconventional superconductivity.

## I. INTRODUCTION

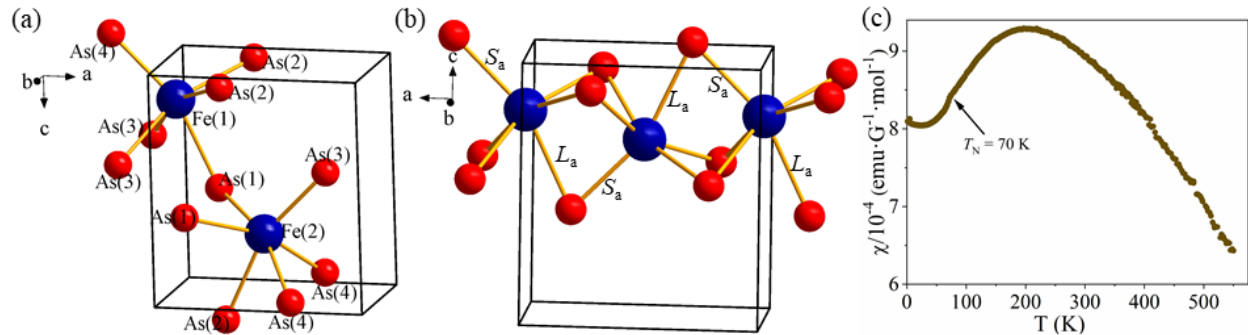
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The iron-arsenide binary, FeAs, can be a template structure for potential iron-arsenide superconductors. While structurally distinct from the iron-arsenide superconductors, FeAs is reported to have an interplay of incommensurate spin-density wave (SDW) and itineracy [1], favoring the highly anisotropic transport and magnetization properties characteristic of the iron arsenide superconductors [2]. The discovery of ferropnictide [3] and chalcogenide [4] superconductors has generated interest in exploring interactions between crystal and magnetic structure, short range correlations, magnetic dynamics and unconventional superconductivity [5, 6]. Understanding the nature of Fe-As bonds and Fe-Fe interactions of this simple iron arsenide binary may therefore help to answer fundamental questions underlying the difference between FeAs-binary and iron arsenide superconductors, which enable both magnetic and Cooper pair interactions.

The FeAs structure is shown in Figure 1. The reported structure is orthorhombic,  $Pnma$  (MnP type) with two unique Fe sites. Earlier attempts to establish the structure of FeAs vacillated on the structure as  $Pnma$  or  $Pna2_1$ , where each Fe would possess slightly different arsenic coordination [7]. Due to the relatively small differences between the two models [7, 8], the slightly higher symmetry  $Pnma$  is traditionally used. No structural transition is reported in the literature prior to the melting point near 1325 K [8]. Figure 1a shows the unit cell with two (out of the total four) distorted  $\text{FeAs}_6$  octahedral units depicted. In the  $Pnma$  configuration, the Fe sits at the  $4c$  Wyckoff position, which results in each site possessing an equivalent set of long, short, and intermediate Fe-As distances. The labels assigned to each atom are derived from our lower symmetry labeling used in the modeling. In this construct, each Fe site has two sets of equal length bonds in the buckled equatorial position, and two significantly longer axial bonds of distinct length which are each slightly distorted away from the central symmetry axis of the octahedron [7]. The face sharing  $\text{FeAs}_6$  octahedra are connected in an alternating network linked through the long axial ( $L_a$ ) and short axial ( $S_a$ ) bond distances, respectively, as shown in Figure 1b. Additionally, these  $\text{FeAs}_6$  octahedra interconnect with each other along  $b$ - and  $c$ - axis via sharing edges.

FeAs is reported to have a non-collinear SDW structure below  $T_N = 70$  K, with incommensurate ordering at 4 K [1]. In the nonmagnetic phase, Mössbauer experiments show lattice-magnetic interactions and anisotropic local susceptibility of Fe above  $T_N$  [9], for which we find additional evidence here. The magnetic susceptibility exhibits broad regions at high-temperatures that may suggest some type of short-range ordering [2], while significant deviations in resistivity are noted between the  $b$ - and  $c$ -axes [2, 10]. In a similar manner to the iron-arsenide superconductors, computational reports on FeAs fail to fully capture the correct static structure and magnetic properties [11, 12], suggesting a role for the subtle local structural effects that we study here.



**Figure 1.** Two views of the FeAs structure: (a) the distorted FeAs<sub>6</sub> octahedra, where Fe ions are six-fold coordinated by As. Bonds belonging to the buckled equatorial plane of each octahedra are of equal length, while the axial bonds are separated into long axial ( $L_a$ ) and short axial ( $S_a$ ) bond distances. (b) The bonding network between the octahedra, where the bonding connections alternate between short and long axial connections along the  $a$ -axis. (c) Magnetic susceptibility of FeAs, showing  $T_N$  at 70 K with a broad anomalous hump centered around 250K.

Moreover, the superconductivity in iron arsenides manifests with doping from metallic parent compounds unlike the cuprates, which exhibit superconductivity near a correlated Mott insulating state. As was pointed out by Paglione and Greene [6], although the origin of Cooper pairing in 2D iron arsenides remains unidentified, a large amount of circumstantial evidence points to magnetic spin fluctuations. Therefore, much work has been done to study spin dynamics in the parent compounds, for example those of  $A\text{Fe}_2\text{As}_2$  ( $A = \text{Ba}, \text{Sr}, \text{Ca}$ ) [15-19],  $\text{NaFeAs}$  [18, 20], and  $\text{FeTe}_{1-x}\text{Se}_x$  [21] (see also a review by Lumsden and Christianson [5]). The observed overall energy scales are about 200-260 meV, suggesting strong effective magnetic exchange couplings in iron arsenides similar to the exchange couplings hallmark to cuprates. Spin waves in iron arsenide superconductors are well defined at low energies, however much broader at energies above 100 meV suggesting that itinerant electrons play an important role. There is no consensus among researchers whether the observed magnetic excitations can be described with a simple Heisenberg Hamiltonian [16, 19], itinerant scenarios [15, 17], or a model that combines both local moment and itinerant electrons [22, 23]. To this end, the spin dynamics in the simplest iron arsenide, the binary FeAs, are of fundamental importance for understanding the interplay between magnetism and 2D spin excitations which could lead to unconventional superconductivity in these materials.

Also, important here are deviations from long-range crystal symmetry observed from local atomic configuration studies, which have been shown to be critical in understanding the behaviors of the iron-arsenide superconductors [13, 14]. Understanding the coupling of the structure to magnetism, and the role of the local environment of Fe in the structure, may provide clues to the rich physics in the future development in this type of research. This is of particular relevance to understanding the suppression of static magnetism and nematic fluctuations. To investigate short-range structural correlations in FeAs, we performed neutron PDF analyses, and find that the variation in octahedral volume around the iron site tracks closely with the anomalous susceptibility data. Additionally, by using inelastic neutron scattering we find evidence that in the vicinity of  $T_N$ , 2D-like spin fluctuations prevail in this 3D crystal structure. Moreover, we find the weakest structural exchanges to be along the  $a$ -axis, suggesting  $bc$ -layered structure motifs at room temperature, contrary to iron-arsenide superconductors that are comprised of  $ab$ -layers separated in the  $c$ -direction.

## II. EXPERIMENTAL DETAILS

### Synthesis

FeAs materials were produced following Saporov, *et. al.* [24]. The FeAs binary phase was synthesized using Fe powder (Alfa Aesar 99.99%) and As pieces (Alfa Aesar 99.99%). In a typical reaction, Fe and As were mixed in 1:1 stoichiometry and loaded into a silica ampoule

before sealing under vacuum. As the first step, the reaction mixture was heated to 700 °C (20 °C/h, dwell 12 hrs). Then, the temperature was raised to 1065 °C (dwell 24 hrs) before furnace-cooling to room temperature. After the reaction, the resulting grey metallic powder was ground inside the glove box. Further detail on the growth method of FeAs single crystals is described in Ref 6. 1.2 g of sample were prepared for the INS experiments, and the purity of the sample was confirmed using powder X-ray diffraction.

### Neutron Diffraction

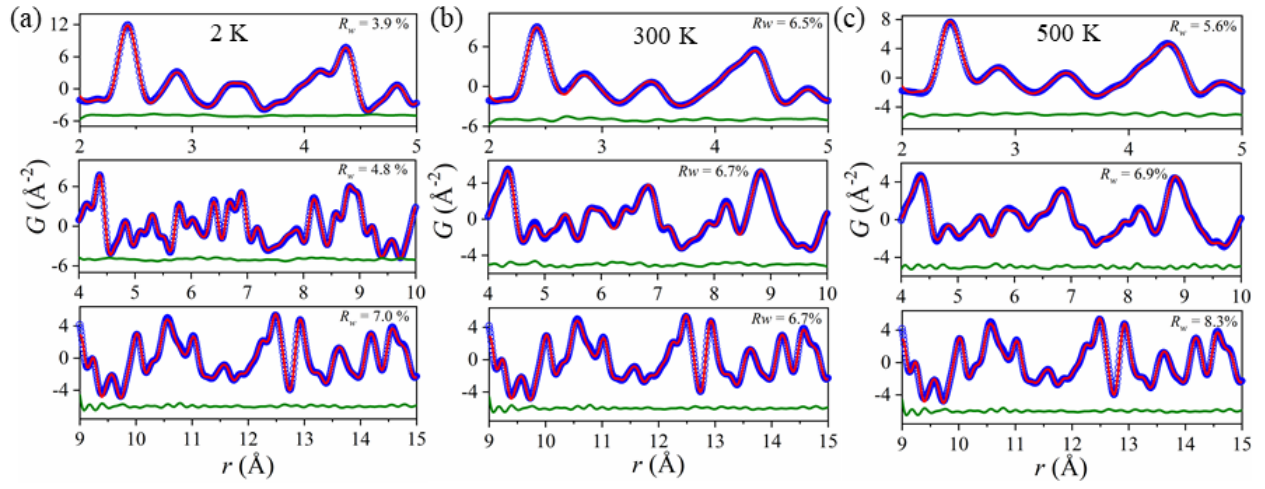
Time of flight neutron powder diffraction data was collected at the Nanoscale Ordered Materials Diffractometer (NOMAD) instrument at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL) [25]. Powdered samples were loaded and sealed into vanadium cans, and data were collected from 2 to 500 K using a liquid-helium cryostat from 2 to 300 K, and a high-temperature displacer for studies above 300 K up to 500 K. Standard calibrations were performed for all instrument setups. Data were reduced using IDL routines, and structural modeling and refinement of structural models against the PDF data was performed using PDFGui [27].

### Inelastic Neutron Scattering

Inelastic neutron scattering measurements were done using the Cold Neutron Chopper Spectrometer (CNCS) [28, 29] and the Fine Resolution Chopper Spectrometer (SEQUOIA) [30] at SNS. Data were collected using fixed incident neutron energies of 81.8 meV for SEQUOIA, and 10.0 meV (3.1 meV) for CNCS, which allowed for the measurement of excitations up to energy transfers of  $\hbar\omega$  65 meV (SEQUOIA) and 8 meV (CNCS). In these configurations, a full width at half maximum (FWHM) resolution of 4.1 meV (SEQUOIA) and 0.06 meV (CNCS) was obtained at the elastic position. The FeAs crystal was mounted in the H0L scattering plane. Measurements were conducted on SEQUOIA at temperatures ranging from 5-90K, while on CNCS measurements are performed from 1.5-90 K. The excitation spectra were recorded by making full 360 degrees rotations with one-degree step. The MantidPlot [26] and Dave [31] software packages were used for data reduction and analysis.

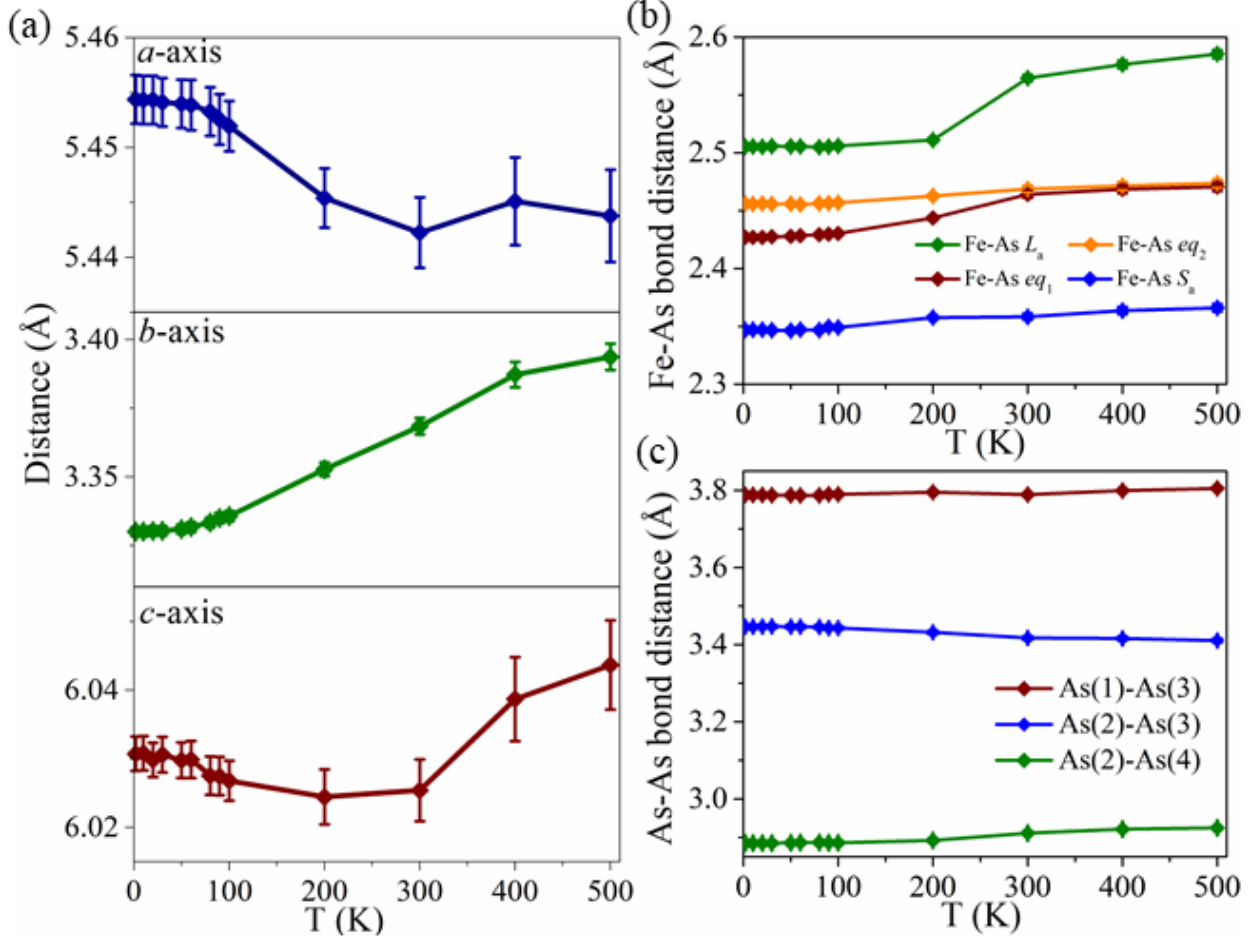
## III. RESULTS AND DISCUSSION

Modeling of PDF data employed the starting structure of *Pnma*, which was found to be a reasonable overall match to the data, with some discrepancies at the local (low real space range) correlations. Congruence of the model and data were improved by forcing the *PI* symmetry condition and using *r* dependent fitting ranges. Representative data from 2, 300, and 500 K are shown in Figure 2. Model refinements included the lattice parameters, Fe and As positions within the unit cell, and the isotropic atomic displacement parameters. The three *r* ranges employed include a region from 2-5 Å which corresponds to the short-range correlations and atomic environments of the individual octahedra, 4-10 Å, which represents the inter-octahedral environment, and 9-15 Å for longer range correlations between octahedral units.



**Figure 2.** Representative PDF data and *P1* model fits for 2, 300, and 500 K data as a function of fitting range  $r$ . Experimental data are shown as blue circles, modeled PDF as red lines, and green lines the model-data residual.  $R_w$  values reflect the model goodness-of-fit.

Temperature dependent lattice parameters and bond distances extracted from the short-range fitting results are shown in Figure 3. The lattice parameter measurements as a function of temperature are consistent with literature studies, with the  $c$ - and  $a$ -axes contracting until 300 K, and the  $b$ -axis showing continuous growth, Figure 3a [2, 24]. Fe-As distances depicted in Figure 3b are extracted from the short-range fitting data describing the intra-octahedral coordination. The axial Fe-As bonds describe the distance of the apical As to the central Fe of the octahedra, with alternating orientation of short and long axial bonds above the equatorial plane for adjacent octahedra. The temperature dependent evolution of the Fe-As axial bonds show continual increase as a function of temperature, with a sharp rise between 200-300 K. Correspondingly, there is a steady increase in the length of the equatorial bonds in the distorted central plane of the octahedra. Taken together, these increasing bond distances demonstrate a steady increase in the octahedral volume surrounding the Fe ion, which reaches a maximum distortion at  $\sim 250$  K, corresponding to the peak in anomalous magnetization shown in Figure 1c. Similar information about the relative orientation of the octahedra is obtained from the As-As distances derived from the short-range PDF models, Figure 3c. The value of the distance between As(2) and As(3) (Figure 1) corresponds to the distance from apical As of one octahedral unit to the equatorial As of the neighboring unit, demonstrating a relative tilt of the octahedral units as the temperature is raised. The Fe-Fe distances (not shown here), also indicate that the Fe-Fe distance between octahedral units along the  $c$ -axis are most highly dependent on temperature, compensating for the increasing canting of the relative Fe-As octahedral units. Fitting results from the higher- $r$  range modeling depicted in Figure 2 indicate similar, though somewhat less pronounced, temperature dependent structural trends. These highlight the local nature of the structural distortions.



**Figure 3.** (a) Change of unit cell parameters with temperature. (b) Temperature dependence of Fe-As short axial ( $S_a$ ), long axial ( $L_a$ ) and equatorial ( $eq_1$ ,  $eq_2$ ) bonds. (c) Temperature dependence of As-As bond distances (using the labeling in Figure 1). All the parameters were derived from the PDF models resulting from 2-5 Å range fits to data.

Closely related to these structural features is the highly anisotropic thermal expansion, including negative thermal expansion (NTE) between 0 and 300 K in both the  $a$ - and  $c$ -axes and a substantial *positive* thermal expansion – some 1.2% – along the  $b$ -axis. In particular, it is notable that the onset temperature of the NTE – between 250 and 300 K, is very close to the temperature of the susceptibility maximum – not the Neel temperature. Previous work on the spinel  $\text{LiGaCr}_4\text{S}_8$  [32] finds an NTE whose onset temperature of approximately 100 K matches the deviation of the susceptibility from  $1/T$  behavior, although in that cubic material the NTE is of course isotropic. Here in this relatively complex 3D structure there is an equally complex NTE behavior.

In our first principles calculations, as in previous work by one of us, the Fe-Fe exchange interactions in the calculated ground state are antiferromagnetic for Fe-Fe neighbors roughly along the  $a$ - and  $c$ - axes, but ferromagnetic along the  $b$ -axis. In fact, despite this relatively large third nearest-neighbor Fe-Fe distance (3.375 Å at 300 K), it was found not possible to stabilize a state with antiferromagnetic interactions along the  $b$ -axis, which suggests some degree of itinerant character here, despite the finding of a substantial local moment in the calculations.

Here we have used the plane-wave density functional theory code WIEN2K [33], within the generalized gradient approximation of Perdew, Burke and Ernzerhof [34].

We also note that the thermal expansion along the  $b$ -axis is rather large – a 1.2% increase, relative to  $T = 1.5$  K at 300 K. Indeed, previous data [35] find a 6.5% increase in this axis at 1300 K, while the corresponding 1300 K increase for the  $a$ -axis is less than 0.5%. Clearly the complex 3D structure is driving these differences in thermal expansion, which is further affected by the appearance of magnetism at low temperature.

It is noteworthy that the NTE only occurs for the directions in which antiferromagnetic interactions are dominant, while the normal and substantial positive thermal expansion occurs in the direction

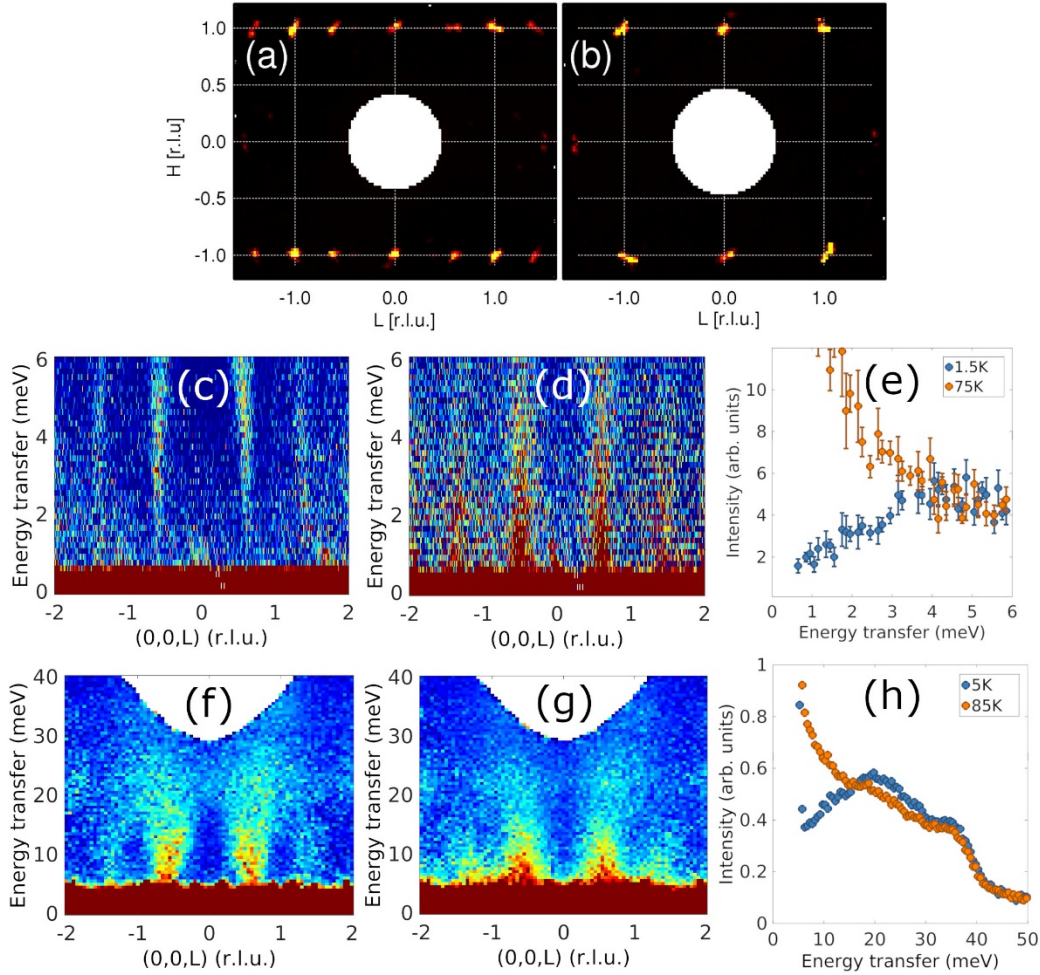
of ferromagnetic interactions. When one combines this with the previous observation [11] that the distance dependence of exchange interactions does not follow the usual monotonic decrease with distance, along with the tantalizing correspondence of the susceptibility maximum temperature with the onset of NTE, one is left with a strong sense that all these unusual facts are somehow related, and that the NTE ultimately originates from the onset of magnetism and the detailed interaction of the magnetic energetics with the more common energies such as the phonon free energy.

Returning to the magnetic order itself, the neutron diffraction scattering map on the single crystal sample at  $T = 1.5$  K confirms incommensurate magnetic order, Figure 4(a,b). At low temperature, Figure 4(c) and Figure 5(a), the spin excitation spectrum is 3D and gapped, with an incommensurate modulation vector  $q \sim 0.4c^*$ , consistent with results from the literature [1]. Above  $T_N$ , Figure 4(d) and Figure 5(b), the spin excitations go from gapped to gapless, reflecting a transition to a two-dimensional state exhibiting short range magnetic order. Our data suggests that the spin-wave bandwidth of FeAs,  $\sim 35$  meV, is considerably reduced from that of iron-arsenide superconductors which is around 200-250 meV [35]. It is known that in iron pnictides AFM fluctuations remain into the paramagnetic phase region above  $T_N$ , where long-range order is already absent [5, 32]. What comes as a surprise is an apparent shape of the magnetic excitations. As one can see in the constant energy slice, the magnetic excitations become anisotropic at  $T = 90$  K (Figure 5). The magnon intensity extends in the  $H$  direction and forms stripes, reflecting a collapse of coherence along  $a^*$ , while remaining coherent along  $c^*$ . Unlike the undoped 2D parents of iron-arsenide superconductors, where the magnetic correlations are considerably weaker along the  $c$ -axis than in the  $ab$ -plane, inelastic neutron scattering here shows that the spin fluctuations in the 3D FeAs binary are nearly 2D in the  $bc$ -plane at 90 K. This observation is further supported by the nature of FeAs<sub>6</sub> connectivity in FeAs structure where FeAs<sub>6</sub> share edges along the  $bc$ -plane while face shared along the  $a$ -axis. The edged sharing nature of the FeAs<sub>6</sub> octahedra could facilitate a pseudo 2D Fe-Fe lattice in the 3D FeAs structure.

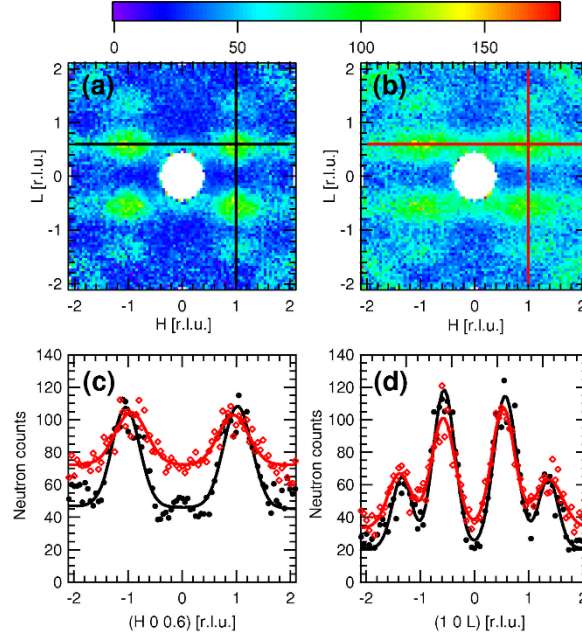
Thus, we find the steady change observed in octahedral volume and relative octahedral tilting as a function of temperature via PDF track closely the anomalous magnetization measurements, with the maximal adjustment to the octahedral volume occurring near the maximal value for magnetization. The apical As within the FeAs<sub>6</sub> octahedra diverging to generate two distinct bond distances, and the equatorial As ions continually expanding, is reflective of a continuous Jahn-



Teller type distortion. The subsequent octahedral tilt reflects the retained coherence along the  $c^*$  direction up to 90 K as observed in the INS data.



**Figure 4.** Elastic neutron scattering map of FeAs at temperature (a)  $T = 1.5$  K and (b)  $T = 75$  K in the  $(H0L)$  scattering plane. (c) Low-energy part of magnetic excitations along the  $(10L)$  direction taken at CNCS at  $T = 1.5$  K, (d)  $T = 75$  K. The intensity is averaged over an interval of  $\pm 0.05$  r.l.u. in the H and K directions. (e) The energy cuts at the AFM wave vector at  $T = 75$  K, indicating the opening of the spin-wave energy gap at low temperature. (f) The INS spectra taken at SEQUOIA in the  $(10L)$  direction at  $T = 5.0$  K, and (g)  $T = 85$  K, i.e. in the AFM and paramagnetic state. The intensity is averaged over an interval of  $\pm 0.1$  r.l.u. in the H and K directions. (h) Energy dependence of the inelastic signal integrated within one Brillouin zone for  $T = 5$  and 85 K, demonstrating the spin-wave bandwidth of FeAs is  $\sim 35$  meV. For better energy coverage and statistics we symmetrized the data according to the crystal symmetry before integration.



**Figure 5.** Constant energy transfer  $\hbar\omega = 12$  meV slices in the  $(H0L)$  plane taken at SEQUOIA at temperatures (a)  $T = 5.0$  K, and (b)  $T = 90$  K. Inelastic features at the corners around  $\mathbf{q} = (\pm 2 \ 0 \ \pm 2)$  are phonons. (c) and (d) Q-dependence of the spin wave excitations below (filled black circles) and above (open red diamonds)  $T_N$  obtained through constant energy cut as shown by solid lines in the upper panels. Lines are guide to the eyes for the observed scattering.

#### IV. CONCLUSION

To summarize, we present correlation between changes in the local structure and the magnetic susceptibility of FeAs. According to PDF analysis of short-range correlations, lattice parameters and bond distances increase overall with temperature, but in a complex and non-linear way. In particular, the axial Fe-As bond distances increase with temperature revealing an overall FeAs<sub>6</sub> octahedral volume increase. Further, the FeAs<sub>6</sub> octahedral volume increases sharply between 200-300 K, which can be directly related to the magnetic susceptibility  $\chi(T)$  result, which shows an anomalous broad feature up to 550 K, with  $\chi$  continuing to increase above the Néel antiferromagnetic ordering temperature ( $T_N = 70$  K), peaking at  $\sim 250$  K, then decreasing gently above. Additionally, we carried out a detailed INS mapping of  $S(\mathbf{Q}; \hbar\omega)$  of magnetic excitations throughout reciprocal space at temperatures above and below the antiferromagnetic transition  $T_N$ . At low temperatures we observe gapped steeply dispersing anisotropic 3D spin waves extending to  $\sim 35$  meV at zone boundaries. This is similar to the anisotropic 3D spin excitations observed in the superconducting iron-arsenide compounds, albeit those occur at much higher energy scale. Above  $T_N$ , the spin excitations become quasi-2D in both FeAs and superconducting iron-arsenide parent compounds like BaFe<sub>2</sub>As<sub>2</sub>. One thus expects a dimensional crossover from 2D magnetic fluctuations at elevated temperatures to 3D spin waves at ground state. The consequence of doping such a compound, and its potential to achieve unconventional superconductivity is yet to be tested.

#### IV. ACKNOWLEDGEMENT

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