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Formation of As-As Interlayer Bonding in the collapsed tetragonal phase of NaFe_2As_2 under pressure

SUBJECT AREAS:

SUPERCONDUCTING
PROPERTIES AND
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NaFe_2As_2 is investigated experimentally using powder x-ray diffraction and Raman spectroscopy at pressures up to 23 GPa at room temperature and using ab-initio calculations. The results reveal a pressure-induced structural modification at 4 GPa from the starting tetragonal to a collapsed tetragonal phase. We determined the changes in interatomic distances under pressure that allowed us to connect the structural changes and superconductivity. The transition is related to the formation of interlayer As-As bonds at the expense of weakening of Fe-As bonds in agreement with recent theoretical predictions.

Nature of superconductivity in iron-based superconductors (FeSCs) remain a challenge of modern condensed matter physics due to the complicated interplay between their structure, magnetism, electronic nematicity, and superconductivity^{1,2}. A generic picture for the early discovered sister cuprate system is that superconductivity emerges and develops in a dome in the charge carrier concentration versus temperature phase diagram when magnetism of a parent compound is suppressed and a narrow spin glass state³ is passed. To study the emergence of superconductivity, one can naturally apply chemical doping, however application of pressure has the similar effect in FeSCs as there are some similarities for the structural distortions between pressure and chemical doping⁴. In the case of 122 FeSCs, pressure-induced suppression of antiferromagnetic spin fluctuations was proposed to account for the disappearance of superconductivity in a so-called collapsed tetragonal (CT) phase⁵. However, the structural modification has been suggested to be a key to the understanding of the superconductivity of iron pnictides⁶. A common structural characteristic of all Fe SCs is the presence of As-Fe-As layers forming edge-sharing FeAs_4 tetrahedra. It is believed that superconductivity emerges from these layers^{1,2}.

NaFe_2As_2 crystallizes in the tetragonal (T) ThCr_2Si_2 -type structure ($I4/mmm$)^{7,8} (see Fig. 1), belonging to the so-called 122 family of FeSCs. It has been characterized as the “missing” member of the 122 system, since initially it was thought that Na, due to its small ionic radius, cannot fill the coordination sphere^{7,8} between the As-Fe-As layers. Moreover, NaFe_2As_2 has a remarkably high superconducting transition temperature T_c of 25 K⁸ in comparison with less than 5 K in the case of Cs and Rb within this AFe_2As_2 family.

Previously reported structural studies on 122 FeSCs under pressure (e.g. Ref. 9) were limited to the cases of A being a divalent alkaline earth or rare earth metal atom, while systems with monovalent alkali metal, to the best of our knowledge, have not been studied. Although all previous studies suggested that the transformation from the T to the CT phase is a universal characteristic of divalent AFe_2As_2 compounds¹⁰, a detailed structural study on the atomic level and the link between structural modifications and superconductivity under pressure is still missing. In this paper we present a combined experimental, using x-ray diffraction (XRD) and Raman spectroscopy, and theoretical study of NaFe_2As_2 under pressure. We examine the structural behavior of AFe_2As_2 superconductors under pressure in the case of A being an alkali metal to obtain a deeper insight on the interplay between structure and superconductivity under pressure. We present, for the first time, direct experimental evidence of the

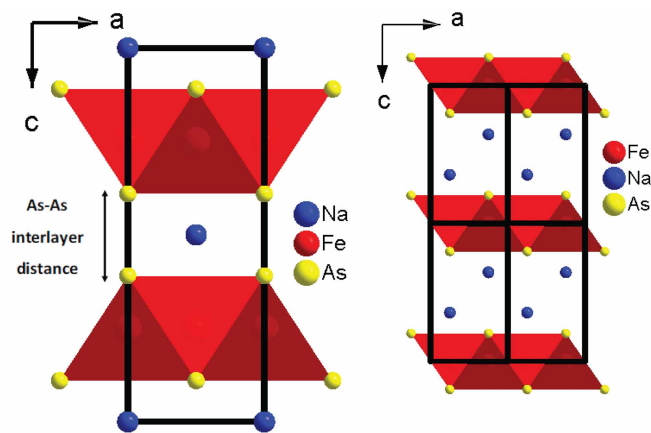


Figure 1 | (a) ThCr₂Si₂-type crystal structure of NaFe₂As₂, (b) PbClF-type crystal structure of NaFeAs.

formation of As-As interlayer bonds under pressure. According to theoretical predictions^{11,12} this is the key parameter determining the correlation between structure and superconductivity for 122 SC.

Results

X-ray diffraction results and analysis. Figure 2 shows selected XRD patterns of NaFe₂As₂ obtained at various pressures up to 23 GPa. All the observed peaks in this pressure range can be properly indexed according to the tetragonal ThCr₂Si₂-type structure. On the other hand, an unusual pressure behavior of the Bragg peaks related with the *a*-axis can be clearly seen at low pressures. This is highlighted by the merge of the (114) and (200) peaks at $2\theta \approx 10^\circ$ and the splitting of the peak at $2\theta \approx 7^\circ$ into its components, (110) and (103). We observe a decrease of the 2θ position of the (200) peak and a practically constant position of the (101) peak, while the 2θ positions of all other peaks [e.g. (002)] shift towards higher values.

In order to determine the positional parameters and the interatomic distances we have performed a detailed Rietveld refinement of the XRD patterns using the GSAS program¹³. Typical refined profiles are shown in Fig. 3 at 1.0 and 5.1 GPa. The only free positional parameter of this structure is the *z* position of As atoms, Wyckoff position (WP) 4e (0, 0, *z*), since positions of Na and Fe atoms are

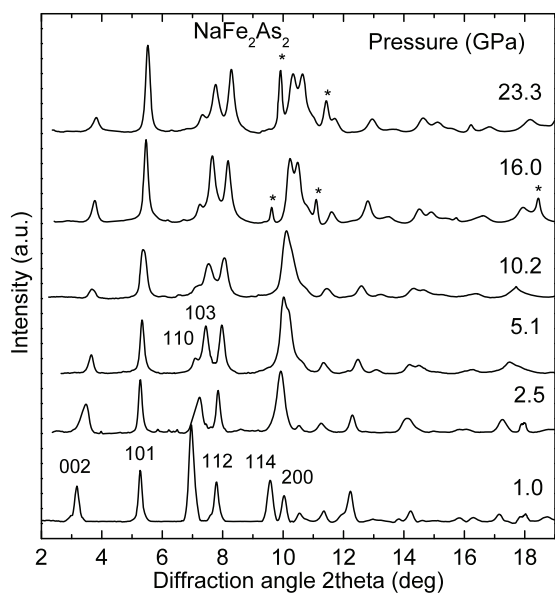


Figure 2 | X-ray diffraction patterns of NaFe₂As₂ at various pressures. The asterisks denote peaks from Ne.

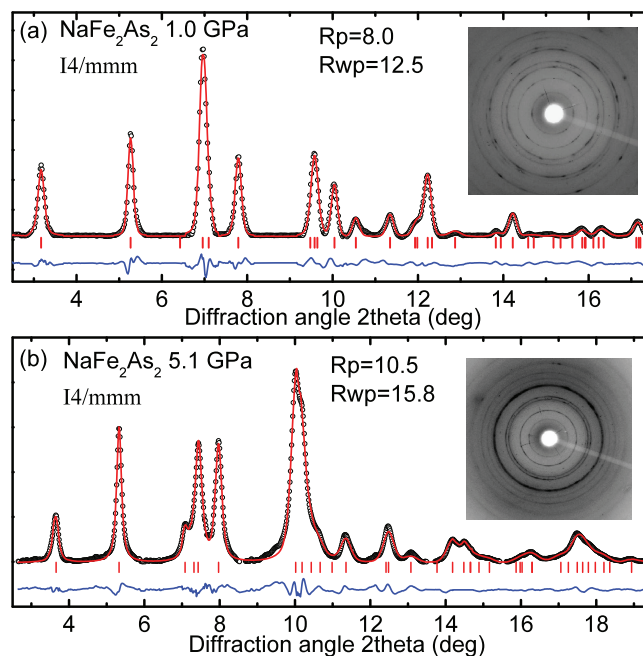


Figure 3 | Rietveld refinements for NaFe₂As₂ at (a) 1.0 GPa and (b) 5.1 GPa. Respective 2D x-ray diffraction images are shown in insets.

fixed. Our two-dimensional (2D) images reveal an almost perfect ring shape of reflections, mainly due to the very fine powder used in this study. In addition, wide angle dispersive XRD measurements helped us to overcome any intensity redistribution caused by preferred orientation. Moreover, XRD patterns have been collected from several spots of the sample at the same pressure, and the results were averaged. The agreement between experimental and theoretical interatomic distances provides an additional confidence of these results.

From XRD data of NaFe₂As₂ we have obtained the lattice parameters and the unit cell volume as a function of pressure, and the results are shown in the plots of Fig. 4. The pressure evolution of the lattice parameters and the *c/a* ratio changes at a critical pressure $P_c \approx 4$ GPa. Below P_c , *a*-axis increases while both the *c*-axis and the *c/a* ratio decrease rapidly. In contrast above P_c , *a*-axis starts to decrease and *c*-axis becomes much less compressible. Consequently the *c/a* ratio shows a gradual decrease. The different behavior of *c*-axis, below and above P_c , can be viewed as a modification of the initial tetragonal phase (T) to the so-called collapsed tetragonal (CT) phase (e.g. Ref. 14). We have fitted the pressure-volume data by the third-order Birch equation of state¹⁵ and determined the bulk modulus B_0 and its first pressure derivative B'_0 (Fig. 4). The CT phase is much less compressible compared to the T phase as B_0 increases by a factor of 5. No apparent volume discontinuity is observed at this isostructural phase transition.

The results from the theoretical predictions are also plotted in Fig. 4 for both a magnetic (M) and a non-magnetic phase (NM). In the case of the M phase, a ferromagnetic configuration has been used and the energy difference from the antiferromagnetic configuration is very small. It is well known that density-functional calculations have a systematic error of several GPa in the equation of state, and a simple constant shift usually brings computed equations of state into close agreement with experiment¹⁶. Here, the theoretical pressures were corrected by 4 GPa. With this correction, an almost perfect agreement between experimental and theoretical values (for both phases) can be clearly seen from Fig. 4. It is noteworthy that the M phase, although it has higher volume at low pressures, is more stable than the NM one, due to the magnetic interactions which result in a (slightly) lower enthalpy up to well above P_c . Moreover,

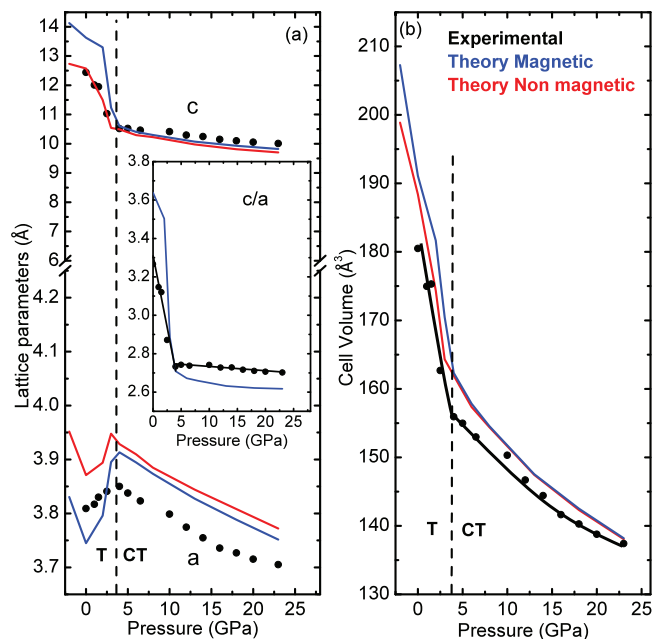


Figure 4 | Pressure dependence of (a) lattice parameters and (b) cell volume of NaFe_2As_2 . The inset shows the pressure dependence of the c/a ratio. Experimental data are shown with solid symbols and theoretical predictions (shifted by 4 GPa to higher P, see text) with blue (M-phase) and red (NM-phase) lines, respectively. The solid black curves in (b) are the third-order Birch-Murnagan EOS fits for the T ($B_0 = 22$ GPa, $B = 4$) and CT ($B_0 = 110$ GPa, $B = 4.5$) phases.

both phases exhibit a T to CT transformation at the same pressure. In the magnetic case (which corresponds to observations of Ref. 7) our calculations suggest that CT phase remains ferromagnetic at $T = 0$ K. Since theory predicts the same phase transformation in magnetic and nonmagnetic cases, we can conclude that the structural behavior is not driven by magnetic interactions.

Raman spectroscopy. Raman spectra of NaFe_2As_2 under pressure show three out of four Raman-active zone-center modes predicted from group theory¹⁷: $A_{1g}(\text{As}(z))$, $B_{1g}(\text{Fe}(z))$ and $E_g(\text{As-Fe}(xy))$ and $\text{Fe-As}(xy)$ (Fig. 5(a)). A_{1g} and B_{1g} modes correspond to the displacement of As and Fe atoms along the c -axis, respectively. The two E_g modes correspond to mixed lateral As and Fe

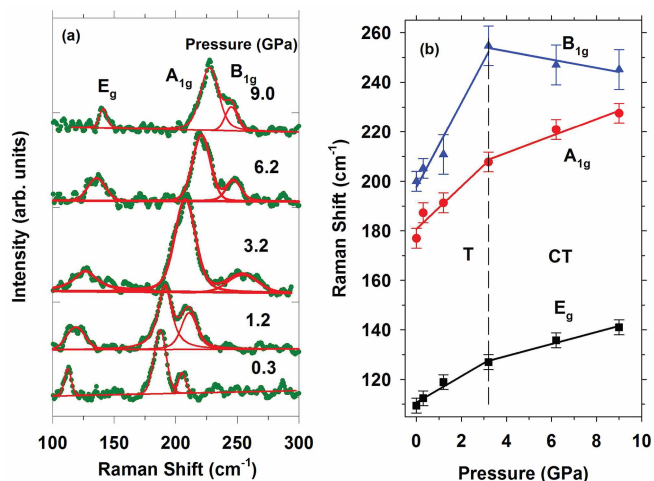


Figure 5 | (a) Raman spectra of NaFe_2As_2 at various pressures. (b) Raman peaks frequencies plotted against pressure. In (b) lines are the results of linear fits.

displacements inside the As and Fe layers. The ambient pressure frequencies are in very good agreement with previous studies¹⁷ with the exception of the very low intensity high frequency $E_g(\text{Fe-As}(xy))$ mode, which was not observed. All Raman modes show normal mode behavior *i.e.* increase of the frequency with increasing pressure in phase T (Fig. 5(b)). At 3 GPa, a critical pressure which is in agreement with that determined from XRD measurements, there is an apparent change in the pressure slope of Raman modes (see Table 1), accompanied by an increase of the linewidth. Remarkably, the $B_{1g}(\text{Fe})$ mode shows a softening in CT phase. The mode Grüneisen parameters (γ_T) determined using the experimental results of this work are shown Table 1. The γ_T parameters of modes of the T phase are common for materials with mixed covalent-ionic bonding (such as within the As-Fe-As layers), due to the presence of weaker interlayer bonds, which experience a larger compression. In the CT phase, the A_{1g} (As) mode exhibit a higher γ_T which almost doubles. These changes suggests an alteration of this mode character from intralayer to interlayer, which results in an increase of the contraction of the respective bond. Similarly, we find the doubling of the γ_T of the intralayer E_g (As-Fe) mode. It is the most intriguing that the γ_T of the B_{1g} (Fe) mode becomes negative, in CT phase suggesting weakening of bonds under pressure.

Discussion

Our x-ray diffraction results reveal the behavior of the As-As interlayer distance in comparison with the Fe-As intratetrahedral distance (see Fig. 6). Figure 7 shows the experimentally and theoretically determined values of these distances under pressure. An almost perfect agreement between the two sets of values is observed. The As-As interlayer distance decreases rapidly with pressure up to 4 GPa. This decrease is almost half of that of c -axis and it accounts for the whole c -axis contraction while the thickness of As-layers (vertical distance between As-As layers of the same As-Fe-As block) remains almost constant or even slightly increases. Shortening of c -axis is driven exclusively by the distance between the tetrahedra blocks ($c = 2d_{\text{As-As}(c)} + 2d_{\text{As-Fe-As}(c)}$). The interlayer As-As and the intralayer Fe-As distances become practically equal above 4 GPa, *i.e.* after the transformation to the CT phase. The As-As distance above 4 GPa takes a value (2.4 Å in experiment and 2.6 Å in theory) which is consistent with the formation of As-As bond (covalent radius of As is 1.2 Å¹⁸). Thus, we conclude that a major change in bonding between As atoms occurs under pressure. It can be viewed as a change from 4-fold to 5-fold coordination with formation of interlayer As-As bonds (see Fig. 6(b)). This conclusion is further justified by the doubling of the γ_T of the A_{1g} mode after the phase transition. In contrast the decrease of the γ_T of the B_{1g} mode indicates weakening of the respective Fe bond.

Previous experimental studies on AFe_2As_2 ($A = \text{Eu}^{10}, \text{Ba}^{19}, \text{Sr}^{20}, \text{Ca}^{14}$) compounds, reveal a common structural trend under pressure. This is an increase of a while both the c and c/a ratio decrease rapidly below P_c , and a decrease of a and much less compressible c above P_c . In the light of this observation, Uhoja *et al.*¹⁰ suggested that the transformation from the T to the CT phase is a universal characteristic of AFe_2As_2 compounds, while the value of P_c depends on the divalent metal. Our study reveal a similar behavior for single valence metal suggesting that this universality is also independent of the valence of A metal. Transformation to the CT phase with further increasing pressure always suppresses¹⁹ or diminishes superconductivity²⁰. In a study of CaFe_2As_2 under pressure¹⁴ it has been suggested that one of the main structural differences between T and CT phases is the value of the As-Fe-As tetrahedral angles. Both tetrahedral angles change abruptly during the phase transition from a value very close (T) to a value far away (CT) from the ideal tetrahedral angle (109.5°). Since T_c decreases with increasing deviation from the ideal tetrahedral angles, it has been concluded that this is crucial for



Table 1 | Assignments, ambient conditions frequencies ω_0 (in cm^{-1}), slopes $(\partial\omega/\partial P)_T$ (in $\text{cm}^{-1}\text{GPa}^{-1}$) and Grüneisen parameters $\gamma_T = -\partial(\ln\omega)/\partial(\ln V)|_T$ of the Raman modes of the T and CT phases

| Mode | T | | | CT | | |
|----------|------------|---------------------------------|------------|------------|---------------------------------|------------|
| | ω_0 | $(\partial\omega/\partial P)_T$ | γ_T | ω_0 | $(\partial\omega/\partial P)_T$ | γ_T |
| E_g | 110.7 | 5.3 | 1.05 | 119.8 | 2.4 | 2.2 |
| A_{1g} | 180.7 | 8.6 | 1.05 | 197.8 | 3.4 | 1.9 |
| B_{1g} | 200.9 | 17.0 | 1.86 | 259.2 | -1.7 | -0.72 |

superconductivity although the direct link and the underlying mechanism which correlates tetrahedral angles and superconductivity is not clear.

Recent theoretical studies^{21,11,12} were focused on the change in interatomic distances under pressure, mainly on the interlayer As-As distance (noted as As-As (c) in Fig. 6). This distance has been predicted to decrease abruptly with pressure, reaching a value that is very close to the As-As covalent bond distance in the CT phase. Consequently it has been proposed that the transition to the CT phase is induced by formation of a direct As-As interlayer bond and a weakening of the in-plane Fe-Fe¹¹ and Fe-As bonds¹². It is noteworthy that in the case of 111 superconductors (e.g. Ref. 22) the Fe-As-Fe layers are separated by two layers of cations (see Fig. 1). Thus, an interaction between As atoms of different layers is hindered and only intralayer modifications can affect superconductivity.

The spin-state of Fe is the key parameter which controls As-As bonding and consequently the lattice parameters¹². Under compression the magnetic moment of Fe decreases and consequently, the strength of the Fe-As bonding (see Fig. 4 of Ref. 12). This is also evident from our calculations, see Fig. 8. The results of our calculations suggest that the CT phase is magnetic *i.e.* the Fe magnetic moment is not vanished but suppressed after the transformation decreasing the strength of the Fe-As bonding in agreement with softening of the B_{1g} Raman mode (Fig. 5). The structural changes determined in this paper (Fig. 7) clearly support this scenario. A direct consequence of the As 5-fold coordination is that the system loses its two-dimensionality (Fig. 6(b)), and with it, superconductivity. Moreover, the weakening of the in-plane Fe-Fe bonds¹¹ in the CT phase also decreases superconductivity.

From our data we find that the tetrahedral angles change continuously with pressure (inset to Fig. 7) in a manner very similar to that determined previously in CaFe_2As_2 ^{14,9} and also predicted by theory¹². During the initial compression the *a*-axis expands and the *c*-axis rapidly decreases due to the development of the As-As interlayer bonding and this keeps Fe-As distances almost constant. In addition,

the tetrahedral angles are close to, or even approach, the ideal value. Above P_c , the tetrahedral angles take value away from the ideal because *a*-axis stops to increase to mediate the *c*-axis decrease. So,

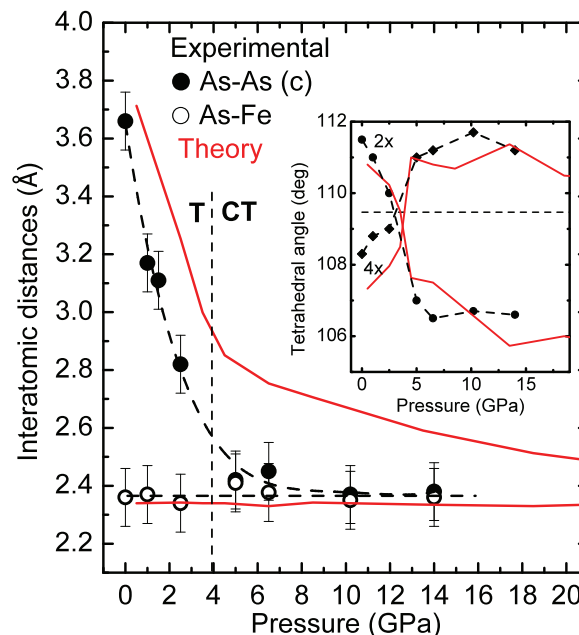


Figure 7 | Pressure dependence of selected interatomic distances of NaFe_2As_2 : As-As interlayer along the *c* axis and Fe-As inside the FeAs_4 tetrahedra. Experimental and theoretical values are shown with black symbols and red lines respectively, the dashed lines are guides for the eye. The inset shows the pressure dependence of the two distinct tetrahedral As-Fe-As bond angles. The ideal tetrahedral angle is indicated by the horizontal dashed line.

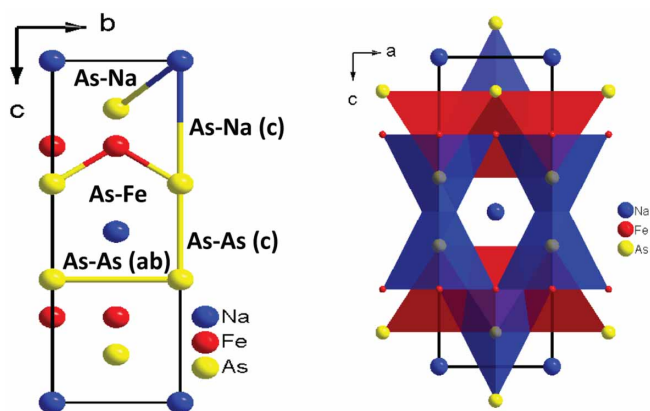


Figure 6 | (a) ThCr_2Si_2 -type crystal structure of NaFe_2As_2 showing the different interatomic distances and (b) ThCr_2Si_2 -type crystal structure of NaFe_2As_2 with As atoms in 5-fold coordination.

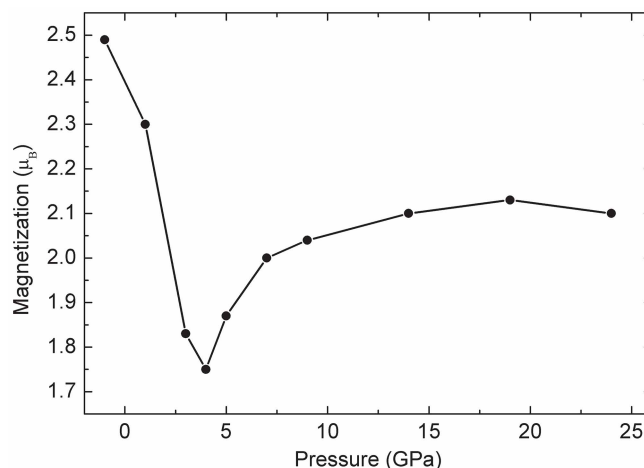


Figure 8 | Calculated magnetization per unit cell of NaFe_2As_2 as a function of pressure.



the correlation between the deviation of tetrahedral angles and T_c turns out to be a “side effect” of the change of As atom position with increasing pressure which primarily affect T_c .

In conclusion, our study reveals, for the first time, the strong experimental evidence supporting the theoretically suggested mechanism controlling the structural behavior of AFe_2As_2 compounds under pressure. Moreover the concomitant experimental and theoretical study of NaFe_2As_2 provides, missing up to now, a direct link between structural characteristics and superconductivity under pressure.

Methods

Experimental study. Fine powder prepared of NaFe_2As_2 single crystals were loaded into a diamond anvil cell (DAC) for the angle dispersive XRD experiments. For the high-pressure Raman measurements, small pieces with a typical dimension of $50\ \mu\text{m}$ were loaded into a DAC. Neon was used as the pressure-transmitting medium for both sets of measurements. Small quantities of ruby and gold powder were also loaded, for determination of pressure through ruby luminescence and gold equation of state (EOS), respectively. XRD data were collected at the GSECARS (sector 13), using a MAR355 CCD detector. The monochromatic x-ray beam ($\lambda = 0.3344\ \text{\AA}$) was focused to a nominal diameter of $4\ \mu\text{m}$. The images were integrated using the FIT2D²³ program to yield intensity versus 2θ diagrams. Raman spectra were measured in a 135° geometry using the $532\ \text{nm}$ line from a solid state laser for excitation. Ultralong fluorescence type Ila synthetic diamond anvils were used for Raman experiments.

Single crystals in the Na-Fe-As system were grown by use of the NaAs flux method. We obtained NaAs by reacting the mixture of the elemental Na and As in an evacuated quartz tube at 200°C for 10 h. NaAs and Fe powders were carefully weighed and thoroughly ground. The mixtures were put into alumina crucibles and then sealed in iron crucibles under $1.5\ \text{atm}$ of highly pure argon gas. The crucibles were sealed and heated to 950°C at a rate of 60°C/h in the tube furnace filled with the inert atmosphere and kept at 950°C for 10 h and then cooled slowly to 600°C at 3°C/h to grow single crystals. The shiny crystals with typical size of $6 \times 6 \times 0.2\ \text{mm}$ can be easily cleaved from the melt.

Theoretical calculations. Our theoretical calculations were performed using density functional theory within the generalized gradient approximation²³ and using the PAW method²⁶ as implemented in the VASP code²⁷. The PAW potentials used had [Be] core (outermost radius 2.2 a.u.) for Na atoms, [Ar] core (radius 2.3 a.u.) for Fe atoms, and [Ni] core (radius 2.1 a.u.) for As atoms. We used the plane wave kinetic energy cutoff of 360 eV and $6 \times 6 \times 3\ \Gamma$ -centered meshes for Brillouin zone sampling. Electronic optimization was done self-consistently with a threshold of $10^{-4}\ \text{eV/cell}$, and structure relaxation proceeded until changes in the enthalpy were below $10^{-3}\ \text{eV/cell}$. A ferromagnetic configuration with all Fe atoms given a starting magnetic moment of 2 Bohr magnetons was used. The starting magnetic moment plays little role (only the magnetic symmetry is important) and was optimized during electronic and structural relaxation.

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Author contributions

E.S., X.-J.C. and A.G. designed the research. E.S. and A.G. conducted the experiments and analyzed the experimental data. A.R.O. performed the calculations. A.F.W., Y.J.Y., X.G.L. and X.H.C. prepared the single crystals NaFe_2As_2 . E.S., X.-J.C., A.G. and A.R.O. contributed in writing the manuscript, all authors reviewed the manuscript.

Additional information

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