Raman scattering study of NaFe$_{0.53}$Cu$_{0.47}$As

W.-L. Zhang,$^{1, *}$ Y. Song,$^{2}$ W.-Y. Wang,$^{2}$ C.-D. Cao,$^{2, 3}$ P.-C. Dui,$^{2}$ and G. Blumberg$^{1, 4, †}$

$^1$Department of Physics & Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA
$^2$Department of Physics and Astronomy and Rice Center for Quantum Materials, Rice University, Houston, Texas 77005, USA
$^3$Department of Applied Physics, Northwestern Polytechnical University, Xi’an 710072, China
$^4$National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia

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We use polarization-resolved Raman scattering to study lattice dynamics in NaFe$_{0.53}$Cu$_{0.47}$As single crystals. We identify 4 $A_{1g}$ phonon modes at 125, 172, 183 and 197 cm$^{-1}$, and 4 $B_{3g}$ phonon modes at 101, 138, 173, 226 cm$^{-1}$. The phonon spectra are consistent with the $Ibam$ group, which confirms that the Cu and Fe atoms form a stripe order. The temperature dependence of the phonon spectra suggests weak electron-phonon and magneto-elastic interactions.

The parent compound of iron-pnictide superconductor, NaFeAs, is a bad metal. It exhibits a tetragonal to orthorhombic transition at 52 K, a paramagnetic to spin-density wave (SDW) transition at 41 K, and a superconducting transition at 23 K [1]. Doping copper into NaFeAs suppresses the orthorhombic and SDW order and enhances superconductivity [2–4]. Recently, it was found that heavy Cu substitution on the Fe site induces Mott-insulator-like behavior [5, 6]. The electronic properties of the heavily doped NaFe$_{1-x}$Cu$_x$As are similar to lightly doped cuprates [5, 7, 8].

For $x > 0.44$ a long-range collinear antiferromagnetic (AFM) order with moment on the Fe sites develops below 200 K. The moment increases with Cu concentration [6]. At the solubility limit near $x = 0.5$, new superlattice peaks appear in the TEM diffraction pattern, which are interpreted as the signature of Cu and Fe stripe order formation [6], as depicted in inset of Fig. 1. Compared to the parent NaFeAs compound in the tetragonal phase, the stripe-ordering of Cu and Fe in heavily-doped NaFe$_{1-x}$Cu$_x$As removes the lattice four-fold rotational symmetry and reduces the crystallographic space group from $Fmmm$ (point group $D_{4h}$) to $Ibam$ (point group $D_{4h}$), making a structural analogue of the magnetic order in NaFeAs.

Here we present polarization-resolved Raman scattering study of the lattice dynamics for NaFe$_{0.53}$Cu$_{0.47}$As single crystals. Four $A_{1g}$ phonon modes at 125, 172, 183 and 197 cm$^{-1}$ and four $B_{3g}$ phonon modes at 101, 138, 173, 226 cm$^{-1}$ are identified. The phonon spectra are consistent with the Fe/Cu stripe-ordered structure. All the observed phonons exhibit Lorentzian line shape. Across the AFM phase transition, no phonon anomaly is observed. The data suggests weak electron-phonon and magneto-elastic interaction.

NaFe$_{1-x}$Cu$_x$As single crystals were grown by self-flux method [6, 9]. The nominal Cu concentration was $x = 0.85$, which resulted in $x = 0.47$ actual concentration [6].

The crystal belongs to $Ibam$ space group at room temperature, as shown in the inset of Fig. 1. The crystallographic principle axis [001] of the $Ibam$ group is along Fe(Cu) stripe direction. We define X, Y and Z axes along crystallographic [100], [010] and [001] axes and $Y’/Z’$ along [011]/[01$ar{1}$] directions (inset Fig. 2(a)).

There are 12 atoms in the primitive unit cell. Group theoretical analysis infers $4A_{1g} + 6B_{1g} + 4B_{2g} + 4B_{3g} + 2A_u + 4B_{1u} + 6B_{2u} + 6B_{3u}$ [10] symmetry decomposition of the 36 phonon modes at the Brillouin center Γ point. All the even $g$ modes are Raman active. The irreducible representations and decomposition of the Raman active modes by symmetry are summarized in Table I.

Raman scattering measurements were performed in a quasi-back scattering setup from natural cleaved (100)
TABLE I. Γ point phonon mode decomposition and the selection rules for Raman-active modes in the *Ibam* group.

| Atom | Wyckoff position | Raman active modes |
|------|------------------|--------------------|
| Na   | 8j               | 2*A₉+2B₁ⱼ+B₂ⱼ+B₃ⱼ |
| Fe   | 4b               | B₁ⱼ+B₂ⱼ+B₃ⱼ         |
| Cu   | 4a               | B₁ⱼ+B₂ⱼ+B₃ⱼ         |
| As   | 8j               | 2*A₉+2B₁ⱼ+B₂ⱼ+B₃ⱼ |

surface. Samples were cleaved in a nitrogen-filled glove bag and immediately transferred to a continuous helium gas flow optical cryostat. We used 1.9 and 2.6 eV excitations from Kr⁺ laser, where the laser was focused into a 50×50 μm² spot on the sample. The power was kept below 10 mW to minimize the laser heating. The estimated local heating was less than 5 K. All temperatures were corrected for laser heating.

The Raman scattering signal was analyzed by a triple-stage spectrometer with the spectral resolution setting at about 2 cm⁻¹. We used scattering geometries μν with μ/ν = Y, Z, Y' and Z', where μν is short for $\tilde{X}(\mu\nu)X$ in Porto’s notation. All spectra were corrected for the spectral response to obtain the Raman scattering intensity $I_{\mu\nu}(\omega, T)$. The Raman susceptibility $\chi''_{\mu\nu}(\omega, T)$ was related to $I_{\mu\nu}(\omega, T)$ by $I_{\mu\nu}(\omega, T) = \chi''_{\mu\nu}(\omega, T)[1 + n(\omega, T)]$, where $n(\omega, T)$ is the Bose factor.

TABLE II. Raman tensor and selection rules for the Raman-active modes for $D_{2h}$ group.

| (001) surface | XX | YY | XY/YX |
|---------------|----|----|-------|
| $A_g$         | $a^2$ | $b^2$ | 0 |
| $B_{1g}$      | 0 | 0 | $d^2/e^2$ |
| (010) surface | XX | ZZ | XZ/ZX |
| $A_g$         | $a^2$ | $c^2$ | 0 |
| $B_{2g}$      | 0 | 0 | $f^2/g^2$ |
| (100) surface | YY/ZZ | YZ/ZY | Y'Y'/Z'Z' |
| $A_g$         | $b^2/c^2$ | 0 | $(b+c)^2$ |
| $B_{3g}$      | 0 | $h^2/i^2$ | $(h+i)^2$, $(h-i)^2$ |

Fig. 1 shows the Raman response in NaFe₀.₅₃Cu₀.₄₇As at 250 K for YY+ZZ and Y'Z'+Z'Y' scattering geometries. We identify all the $A_g$ and $B_{3g}$ phonon modes predicted by group theory: four $A_g$ symmetry modes at 125, 172, 183 and 197 cm⁻¹, and four $B_{3g}$ symmetry modes at 101, 138, 173, and 226 cm⁻¹. All modes show symmetric line shape.

We note that at the same frequency as the $A_g$ phonon modes, some modes with weaker intensity are also observed for the $Y'Z'+Z'Y'$ geometry (Fig. 2). The inten-
In summary, we present polarization-resolved Raman scattering study of NaFe$_{0.53}$Cu$_{0.47}$As single crystals. We observe four $A_g$ and four $B_{3g}$ phonon modes at 125, 172, 183, 197 cm$^{-1}$ and 101, 138, 173, 226 cm$^{-1}$, respectively. The results are consistent with the Ibam group symmetry structure where Fe/Cu atoms form stripe order. No phonon anomaly is observed across the magnetic phase transition between 250 to 50 K, suggesting weak electron-phonon and magneto-elastic interaction.

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* wz131@physics.rutgers.edu
† girsh@physics.rutgers.edu
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