**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,$^{2,1}$ P.-C. Dai,$^2$ C.-Q. Jin,$^{3,4}$ and G. Blumberg$^{1,5,†}$

$^1$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
$^3$Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
$^4$Collaborative Innovation Center of Quantum Matter, Beijing, China
$^5$National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia

(Received 23 April 2018; revised manuscript received 25 August 2018; published 13 September 2018)

We use polarization-resolved Raman scattering to study lattice dynamics in NaFe$_{0.53}$Cu$_{0.47}$As single crystals. We identify four $A_{1g}$ phonon modes, at 126, 172, 183, and 197 cm$^{-1}$, and four $B_{3g}$ phonon modes at 101, 139, 173, and 226 cm$^{-1}$ ($D_{4h}$ point group). The phonon spectra are consistent with the $Ibam$ space 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 magnetoelastic interactions.

DOI: 10.1103/PhysRevB.98.094512

**I. INTRODUCTION**

The parent compound of the iron-pnictide superconductor, NaFeAs, is a “bad metal.” It exhibits a tetragonal-to-orthorhombic transition at 52 K, a paramagnetic-to-spin-density-wave transition at 41 K, and a superconducting transition at 23 K [1]. Doping copper into NaFeAs suppresses both the orthorhombic and the paramagnetic-to-spin-density-wave orders and enhances the superconductivity [2–4]. Recently, it was shown that heavy Cu substitution at 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 those of lightly doped cuprates [5,7,8].

For Cu substitution concentration $x > 0.44$ a long-range collinear antiferromagnetic order with magnetic moments residing only at the Fe sites develops below 200 K. The moment increases with Cu concentration substitution $x$ [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 the inset in 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 fourfold rotational symmetry and reduces the crystallographic space group from $Pmmm$ (point group $D_{4h}$) to $Ibam$ (point group $D_{4h}$), making a structural analog of the magnetic order in parent NaFeAs crystals.

Here we present a 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 126, 172, 183, and 197 cm$^{-1}$, and four $B_{3g}$ phonon modes, at 101, 139, 173, and 226 cm$^{-1}$, are identified. The phonon spectra are consistent with the Fe/Cu stripe-ordered structure. All the observed phonons exhibit a symmetric line shape. Across the antiferromagnetic phase transition, no phonon anomaly is observed. The data suggest weak electron-phonon and magnetoelastic interaction.

**II. EXPERIMENTAL**

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

---

$^*$wz131@physics.rutgers.edu
$^1$Present address: Department of Applied Physics, Northwestern Polytechnical University, Xian 710072, China.
$^†$girsh@physics.rutgers.edu

**FIG. 1.** Raman scattering spectra from NaFe$_{0.53}$Cu$_{0.47}$As single crystal for YY + ZZ and YZ + ZY scattering geometries at 250 K measured with 1.9 eV excitation. The spectral resolution is 2.5 cm$^{-1}$. Inset: NaFe$_{0.53}$Cu$_{0.47}$As unit cell with Cu and Fe collinear stripe order. Arrows at the Fe sites mark magnetic moments.
preparation of the reference LiFeAs single crystal is described in [10].

The NaFe$_{1-x}$Cu$_x$As crystal belongs to the Ibam space group at room temperature, as shown in the inset in Fig. 1. The crystallographic principal axis [001] of the Ibam group is along the Fe(Cu) stripe direction. We define the X, Y, and Z axes along crystallographic [100], [010], and [001] axes and $Y'/Z'$ along the [011]/[001] direction [inset Fig. 2(a)]. There are 12 atoms in the primitive unit cell. Group theoretical analysis infers $4A_g + 6B_{1g} + 4B_{2g} + 4B_{1u} + 2A_u + 4B_{1g} + 6B_{2u} + 6B_{3u}$ [11] symmetry decomposition of the 36 phonon modes at the Brillouin zone center $\Gamma$ 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.

Polarization-resolved low-temperature Raman scattering measurements were performed in a quasibackscattering setup from a natural cleaved (100) surface [12]. Polarizers with an extinction ratio better than 1:500 were employed [13]. Samples were cleaved in a nitrogen-filled glove bag and immediately transferred to an optical cryostat with continuous helium gas flow. We used 1.9 and 2.6 eV excitations from a Kr$^+$ laser, where the laser was focused on a 50 × 50-μm$^2$ spot on the sample. The power was kept below 10 mW to minimize the laser heating. The local laser heating was estimated [14,15] and kept at less than 5 K. All referred temperatures are corrected for the laser heating.

The Raman scattering signal was analyzed with a triple-stage spectrometer with the spectral resolution setting at about 2 cm$^{-1}$. We used scattering geometries $\mu\nu$ with $\mu/\nu = Y, Z, Y'$, and $Z'$, where $\mu\nu$ is short for $X(\mu\nu)X$ 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 $I_{\mu\nu}(\omega, T) = \chi_{\mu\nu}^{(1)}(\omega, T)[1 + n(\omega, T)]$, where $n(\omega, T)$ is the Bose factor.

In Table II we list the Raman tensor for the $D_{2h}$ group and the selection rule for experimentally accessible polarizations [16]. Due to the twin structure [6], the collected signal from the (100) surface is a superposition of Raman scattering intensities from two types of orthogonal domains. For example, the signal for parallel polarized scattering geometry along the crystallographic axes contains the intensity from YY geometry for one type of domain and ZZ geometry for the other type of domain. We denote this scattering geometry YY + ZZ. Similarly, cross-polarized signal along the crystallographic axes contains contributions from YY and ZZ geometries and is denoted YZ + ZY, and cross-polarized signal along the diagonal directions contains contributions from YZ’ + ZY’ scattering geometries and is denoted YZ’ + ZY’.

Following the notation in Table II, we assign all phonons that appear in the YY + ZZ geometry to the $A_g$ symmetry modes, and those appear in the YZ + ZY geometry to the $B_{3g}$ modes.

![Figure 2](image-url)

**FIG. 2.** (a, b) $A_g$-symmetry Raman active phonon modes measured for NaFe$_{0.53}$Cu$_{0.47}$As crystal at (a) 250 K and (b) 50 K in YY + ZZ (blue line) and YZ’ + ZY’ (red line) scattering geometries with 2.6 eV laser excitation and spectral resolution 3.5 cm$^{-1}$. Inset in (a): Top view of the Fe-Cu-As layer for the NaFe$_{0.53}$Cu$_{0.47}$As structure and the YZ-Y’Z’ coordinates. (c) The same $A_g$ phonon modes measured at 250 K with 1.9-eV excitation. (d) Raman spectra from tetragonal LiFeAs crystal at 25 K measured in X’X (blue line) and XY (red line) scattering geometries with 2.6 eV laser excitation. Inset in (d): Left: Zoom-in of the data where the signal for X’X polarization is divided by 100 to demonstrate the lack of detectable leakage into cross polarization. Right: Top view of the Fe-As layer for the LiFeAs crystal structure and the XY-X’Y’ coordinates.
TABLE II. Raman tensor and selection rules for Raman-active modes in the $D_{2h}$ point group.

<table>
<thead>
<tr>
<th>Surface</th>
<th>XX</th>
<th>YY</th>
<th>ZZ</th>
<th>XY/YX</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>$a^2$</td>
<td>$b^2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$B_{3g}$</td>
<td>0</td>
<td>0</td>
<td>$d_i^2$</td>
<td>0</td>
</tr>
<tr>
<td>$A_g$</td>
<td>$b^2/c^2$</td>
<td>0</td>
<td>(b + c)²/4</td>
<td>(b - c)²/4</td>
</tr>
<tr>
<td>$B_{3g}$</td>
<td>0</td>
<td>$h^2/i^2$</td>
<td>(h + i)²/4</td>
<td>(h - i)²/4</td>
</tr>
</tbody>
</table>

III. RESULTS AND DISCUSSIONS

In Fig. 1 we show the Raman response for NaFe0.53Cu0.47As crystals at 250 K for YY + ZZ and YZ + ZY scattering geometries. We identify all the $A_g$ and $B_{3g}$ phonon modes predicted by group theory: four $A_g$ symmetry modes, at 126, 172, 183, and 197 cm⁻¹, and four $B_{3g}$ symmetry modes, at 101, 139, 173, and 226 cm⁻¹. All modes show a symmetric line shape.

We note that at the same frequency as the $A_g$ phonon modes, some modes with a weaker intensity are also observed for the $Y'Z' + ZY'$ geometry for both 2.6 and 1.9 eV laser excitations [Figs. 2(a)–2(c)]. The intensity of the leaking modes is about 10% of the $A_g$ phonon intensity in the YY + ZZ geometry, which is much higher than the experimental polarization extinction ratio. In Fig. 2(d) we show data for the LiFeAs tetragonal structure [17] measured employing the same setup. If the substituted Cu ions at Fe sites were randomly disordered, the NaFe1−xCu,xAs structure would have the same point-group symmetry as the LiFeAs structure. By symmetry, no Raman-active phonons are allowed in the XY scattering geometry for the LiFeAs structure. As we demonstrate in the inset in Fig. 2(d), the leakage intensity for the tetragonal LiFeAs structure is less than a percent.

Based on the Raman scattering selection rules, we can deduce that the leakage intensity is proportional to $(b - c)^2/4$ (Table I), which is a measure of the anisotropic electronic properties between the Y and the Z directions [15]. The observation of leakage is consistent with the suggested formation of a long-range stripe order which breaks the crystallographic fourfold symmetry [6]. The count of observed Raman-active phonons for the NaFe1−xCu,xAs structure also suggests that the size of its primitive cell is four times larger than that for the NaFeAs structure (Table I), therefore, the only possible consistent structure is the Fe-Cu stripe-order phase, as shown in the inset in Fig. 1.

In Figs. 3(a) and 3(b) we show the intensity plot of the Raman response $\chi''(\omega, T)$ for $A_g$ (YY + ZZ) and $B_{3g}$ (YZ + ZY) symmetry channels between 250 and 60 K. All phonons show a symmetric line shape. The number of phonon modes and their line shapes do not change across the antiferromagnetic phase transition at 200 K, suggesting weak magnetoelastic interaction.

We analyze $A_g(1)$, $A_g(4)$, and $B_{3g}(2)$ phonons by fitting to Lorentzian function. As an example, Fig. 3(c) shows the $A_g(4)$ mode at 250 K and its Lorentzian fit. Inset: Spectral resolution. (d–f) Temperature dependence of the phonon peak frequency for the $A_g(1)$, $A_g(4)$, and $B_{3g}(2)$ modes. Vertical error bars are one standard deviation error of the Lorentzian fit. Dashed lines show fits of the phonon frequency and line width to Eqs. (1) and (2).

$$P(\omega, T) = \frac{\omega}{\omega_0^2 - \omega^2} \exp \left( - \frac{\omega^2}{\omega_0^2} \right)$$

$$\omega(T) = \omega_0 - \omega_1 \left[ 1 + \frac{2}{e^{h\omega_0/2k_BT}} - 1 \right]$$

$$\Gamma(T) = \Gamma_0 + \Gamma_1 \left[ 1 + \frac{2}{e^{h\omega_0/2k_BT}} - 1 \right]$$

The fitting results are summarized in Table III.
IV. CONCLUSIONS

We present a polarization-resolved Raman scattering study of NaFe$_{0.53}$Cu$_{0.47}$As single crystals. We observe four $A_g$ and four $B_g$ phonon modes, at 126, 172, 183, and 197 cm$^{-1}$ and 101, 139, 173, 226 and cm$^{-1}$, respectively. The results are consistent with the $Ibam$ space-group symmetry structure, where Fe/Cu atoms form a stripe order.

TABLE III. Fitting parameters for the frequency and line width of the $A_g(1)$, $A_g(4)$, and $B_g(2)$ modes. Units are cm$^{-1}$.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\omega_0$</th>
<th>$\omega_1$</th>
<th>$2\Gamma_0$</th>
<th>$2\Gamma_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g(1)$</td>
<td>128.72 ± 0.07</td>
<td>0.49 ± 0.02</td>
<td>2.06 ± 0.06</td>
<td>0.23 ± 0.02</td>
</tr>
<tr>
<td>$A_g(4)$</td>
<td>201.51 ± 0.06</td>
<td>1.21 ± 0.02</td>
<td>4.67 ± 0.07</td>
<td>0.53 ± 0.03</td>
</tr>
<tr>
<td>$B_g(2)$</td>
<td>143.82 ± 0.07</td>
<td>0.87 ± 0.02</td>
<td>6.4 ± 0.1</td>
<td>0.41 ± 0.04</td>
</tr>
</tbody>
</table>

No phonon anomaly is observed across the magnetic phase transition from 250 to 60 K, suggesting weak electron-phonon and magnetoelastic interaction.

ACKNOWLEDGMENTS

The spectroscopic work at Rutgers was supported by NSF Grant No. DMR-1709161. Sample characterization (W.Z.) was supported in part by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Contract No. DE-SC0005463. The crystal growth at Rice was supported by the US Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012311 and Robert A. Welch Foundation Grant No. C-1839. The growth of LiFeAs crystals at IOPCAS was supported by NSF & MOST of China.

[13] In the setup (see Fig. 2.1 in [12]) a Melles Griot Glan-Taylor polarizing prism with a better than $10^{-5}$ extinction ratio was used to clean the laser excitation beam and a Karl Lambrecht Corporation broad-band polarizing cube with an extinction ratio better than 1:500 was used for the analyzer.