Absence of magnetism in the superconductor \( \text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O} \): Insights from inelastic neutron scattering measurements and \textit{ab initio} calculations of phonon spectra

Mohamed Zbiri,1,* Wentao Jin,2,† Yinguo Xiao,3 Yunlei Sun,4 Yixi Su,2 Sultan Demirdis,2 and Guanghan Cao4

1Institut Laue-Langevin, 71 avenue des Martyrs, Grenoble Cedex 9, 38042, France
2Jülich Centre for Neutron Science JCNS at Heinz Maier-Leibnitz Zentrum (MLZ), Forschungszentrum Jülich GmbH, Lichtenbergstraße 1, D-85747 Garching, Germany
3Jülich Centre for Neutron Science JCNS and Peter Grünberg Institut PGI, JARA-FIT, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
4Department of Physics, Zhejiang University, Hangzhou 310027, China

(Rceived 29 January 2017; revised manuscript received 30 March 2017; published 1 May 2017)

Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O is a self-doped superconductor exhibiting a \( T_c \sim 21.5\) K and containing, distinctively with respect to other Fe-based superconductors, not only \([\text{Fe}_2\text{As}_2]\) layers but also conducting \([\text{Ti}_2\text{O}]\) sheets. This compound exhibits a transition at \( T^* \sim 125\) K, which has tentatively been assigned in the literature to a possible density-wave order. However, the nature of this density wave (whether it is charge- or spin-induced) is still under debate. Magnetism in Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O has never been experimentally confirmed, which raises the question whether this superconductor might be nonmagnetic or exhibiting a very weak magnetism. Here, we report evidence from inelastic neutron scattering (INS) measurements and \textit{ab initio} calculations of phonon spectra pointing towards a possible absence of magnetism in Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O. The INS measurements did not reveal any noticeable magnetic effects in Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O, within the accessible \((Q, E)\) space. The effect of magnetism on describing phonon spectra was further investigated by performing \textit{ab initio} calculations. In this context, nonmagnetic calculations reproduced well the measured phonon spectra. Therefore, our results indicate a nonmagnetic character of the superconductor Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O.

DOI: 10.1103/PhysRevB.95.174301

I. INTRODUCTION

The discovery of high-temperature superconductivity (HTSC) in the Fe-pnictide materials \cite{1,2} paved the road for a tremendous progress towards the understanding of the phenomenon of superconductivity and its interplay with magnetism \cite{3–11} and phonon dynamics \cite{12–23} in these systems. The emergence of HTSC in the Fe-pnictides can either be induced chemically by a targeted doping of a parent compound \cite{24–26} or mechanically by applying external pressure \cite{27,28}. However, recently, HTSC was discovered in a new iron-based oxypnictide superconductor Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O \((22241)\), exhibiting a bulk SC at \( T_c \sim 21.5\) K, and interestingly, subjected to an effective self-doping property \cite{29–32}. This offers an alternative and efficient route for inducing superconductivity, instead of achieving it mechanically or chemically via element substitution. The self-doping stems from an interlayer electronic interaction since this compound contains not only \([\text{Fe}_2\text{As}_2]\) layers but additionally another conducting \([\text{Ti}_2\text{O}]\) sheets, which makes it very distinctive. For this material, a transition at \( T^* = 125\) K has been identified from the electrical resistivity and magnetic susceptibility measurements \cite{25}. It was tentatively ascribed by Raman scattering and optical spectroscopy studies to a possible density-wave (DW) transition in the Ti sublattice \cite{33,34}. Further, Mössbauer measurements did not evidence the occurrence of any long-range magnetic ordering below the \( T^* \) originating from the Fe sublattice in Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O \cite{35}.

Previous studies on different oxygen-free Fe-based superconductors, as well as oxypnictides, highlighted the possibility that the Cooper pairing could be mediated by exchange of antiferromagnetic spin fluctuations \cite{7–11}. However, the presently studied superconducting compound, Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O, seems not to be subject to such magnetic effect. Inelastic neutron scattering (INS) offers a unique tool to probe phonon dynamics over the full Brillouin zone, without any selection rule, which helps exploring phonons and their possible coupling and/or interplay with magnetic degrees of freedom. In this context, we have previously studied different Fe-based pnictides using INS to collect phonon spectra, and in a synergistic way our neutron data were systematically accompanied by \textit{ab initio} lattice dynamical calculations for the sake of the analysis and interpretation \cite{36–38}. Our previous works allowed us to contribute in building up a spin-phonon picture of the previously discovered Fe-based superconductors by establishing the occurrence of spin-lattice coupling. In this paper, we aim at pursuing our work on phonon dynamics in Fe-pnictides by combining INS and \textit{ab initio} calculations to measure and simulate, respectively, phonon spectra of Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O. To the best of our knowledge, only the zone-center phonons of Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O have been studied via Raman spectroscopy \cite{33}.

The aim of this paper is twofold: (i) perform INS measurements to collect phonon spectra—generalized density of states \cite{39,40}—of Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O over an extended temperature range \((2–300\) K\) in order to explore any signature of DW that could be observed and (ii) carry out \textit{ab initio} lattice dynamical calculations to reproduce phonon spectra and therefore gain some insights into the effect of neglecting or considering spin polarization on describing phonon spectra in Ba\(_2\)Ti\(_2\)Fe\(_2\)As\(_4\)O.
This paper is organized as follows. The experimental and computational details are provided in Sec. II and Sec. III, respectively. Section IV is dedicated to the presentation and discussion of the results, and conclusions are drawn in Sec. V.

II. EXPERIMENTAL DETAILS

The polycrystalline sample of Ba$_2$Ti$_2$Fe$_2$As$_4$O was synthesized by solid-state reaction method, as described in Ref. [29] and displays similar macroscopic properties, as the annealed sample as reported there. The quality of the powder sample was checked by x-ray diffraction (XRD) on a Huber x-ray diffractometer with CuK$_\alpha$ radiation at room temperature. The Rietveld refinement of the diffraction pattern at 300 K [Fig. 1(a)] reveals that a minor phase of BaFe$_2$As$_2$ (122, 4.9%) coexists with the 2241 main phase (95.1%) in the sample. In addition, the XRD pattern of the sample was also collected at low temperatures using a cryostat. Even at 13 K, which is the lowest temperature value we could reach, the 22241 main phase still adopts the same space group, $I4/mmm$, as at room temperature. The XRD pattern at 13 K [Fig. 1(b)] can be well refined using the same structure model of the main phase. The temperature dependence of the lattice constants, $a$ (b) and $c$, of the 22241 phase are plotted in Fig. 1(c). Both $a$ and $c$ show a clear kink around the superconducting transition temperature, $T_c$. In addition, for the in-plane lattice constant, $a$, a tiny hump is observed around $T^*$. This might be due to a slight structural modulation associated with the DW transition in the Ti sublattice, as revealed by Raman scattering and optical spectroscopy studies [29,32].

The temperature-dependent INS measurements were performed at the Institut Laue-Langevin (ILL) (Grenoble, France) on ∼1 gram powder sample of Ba$_2$Ti$_2$Fe$_2$As$_4$O. We used the thermal neutron time-of-flight spectrometer IN4C to collect phonon spectra in the temperature range 2–300 K, in the down-scattering regime (neutron energy-loss mode), using different incident neutron wavelengths $\lambda_i = 1.11 \, \text{Å} (E_i = 66.4 \, \text{meV})$, $1.45 \, \text{Å} (E_i = 38.9 \, \text{meV})$, or $2.22 \, \text{Å} (E_i = 16.6 \, \text{meV})$. The data treatment and analysis was done using standard ILL procedures and software tools. Standard corrections including detector efficiency calibration and background subtraction were performed. Contribution from an empty aluminium container was subtracted. A standard vanadium sample was used to calibrate the detectors.

The $Q$-averaged, one-phonon generalized phonon density of states (GDOS) was obtained using the incoherent approximation in the same way as in previous works dealing with phonon dynamics in Fe-pnictides [36–38]. In the incoherent one-phonon approximation, the measured scattering function $S(Q, E)$, as observed in inelastic neutron experiments, is related to the GDOS $g^{(n)}(E)$, as seen by neutrons, as follows [41,42],

$$g^{(n)}(E) = A \left( \frac{e^{2W(Q)}}{Q^2} \frac{E}{n_T(E)} + \frac{1}{2} \pm \frac{1}{2} S(Q, E) \right), \quad (1)$$

with

$$g^{(n)}(E) = B \sum_i \left\{ \frac{4\pi b_i}{m_i} \right\} \chi_i g_i(E), \quad (2)$$

where the + or – signs correspond to energy loss or gain of the neutrons, respectively, and $n_T(E)$ is the Bose-Einstein distribution. $A$ and $B$ are normalization constants and $b_i, m_i, x_i$, and $g_i(E)$ are, respectively, the neutron scattering length, mass, atomic fraction, and partial density of states of the $i$th atom in the unit cell. The quantity between $<>$ represents suitable average over all $Q$ values at a given energy. The $2W(Q)$ is the Debye-Waller factor. The weighting factors for various atoms in the units of barns/amu are as follows [43]: O: 0.2645; Ti: 0.0908; Fe: 0.2081; As: 0.0734; and Ba: 0.0246.

In addition, polarized neutron diffraction measurements were performed at the diffuse scattering cold-neutron spectrometer DNS [44] at the Heinz Maier-Leibnitz Zentrum (Garching, Germany), with an incident wavelength of 4.544 Å.

![FIG. 1. The XRD refinement pattern for the polycrystalline sample at 300 K (a) and 13 K (b). The vertical bars at the bottom indicate the Bragg reflection positions from the Ba$_2$Ti$_2$Fe$_2$As$_4$O main phase and the BaFe$_2$As$_2$ minor phase, respectively. The lowest curve is the difference between the observed and the calculated patterns. (c) The temperature dependence of the lattice constants, $a$ (b) and $c$, of the 22241 phase. The dashed vertical lines mark the superconducting transition ($T_c$) and the density-wave transition ($T^*$).](174301-2)
FIG. 2. The dynamic structure factor $S(Q, E)$ for Ba$_2$Ti$_2$Fe$_2$As$_4$O at 2 K [(a), (c), and (e)], and 300 K [(b), (d), and (f)]. Three incident energies were used: (a) and (b) $E_i = 66$ meV ($\lambda_i = 1.11$ Å), (c) and (d) $E_i = 39$ meV ($\lambda_i = 1.45$ Å), and, (e) and (f) $E_i = 17$ meV ($\lambda_i = 2.22$ Å).

The polycrystalline sample was put inside a thin aluminum sample container that was fixed to the cold tip of the sample stick of a $^4$He close cycle cryostat. Data were collected for 49 hours at 30 K and 16 hours at 150 K, respectively. The polarization analysis was performed via the XYZ method [45], by which the nuclear coherent, spin incoherent, and magnetic scattering cross sections can be separated.

### III. COMPUTATIONAL DETAILS

The starting Ba$_2$Ti$_2$Fe$_2$As$_4$O structure used in the calculations was the experimentally refined one under the tetragonal phase ($a = b = 4.0276$ Å and $c = 27.3441$ Å); with two formula units (22 atoms) per unit cell [29]. The refined structure (space group $I4/mmm$ [$D_{174h}$]), contains six crystallographically inequivalent atoms (one Ba, two As, one
Fe, one Ti, and one O). In order to determine appropriately all force constants, the supercell (SC) approach was used for the lattice dynamics calculations. Thus, a $3 \times 3 \times 1$ SC was constructed ($a^\text{SC} = b^\text{SC} = 12.0828$ Å and $c^\text{SC} = 27.3441$ Å), containing 18 formula units (198 atoms).

Calculations were performed using the projector-augmented wave formalism [46,47] of the Kohn-Sham density functional theory [48,49], within the generalized gradient approximation (GGA), implemented in the Vienna \textit{ab initio} simulation package (VASP). [50] The GGA was formulated by the Perdew-Burke-Ernzerhof (PBE) density functional [51]. The valence electronic configurations of Ba, As, Fe, Ti, and O as used for pseudopotential generation are $5s^25p^6$, $3d^34s^1$, $3d^34s^1$, and $2s^22p$ [4], respectively. The Gaussian broadening technique was adopted, and all results were well converged with respect to $k$-mesh and energy cutoff for the plane wave expansion. A plane wave energy cutoff of 600 eV was used, and the integrations over the Brillouin zone were sampled on a $6 \times 6 \times 2$ grid of $k$-points generated by the Monkhorst-Pack method [52] for the SC phonon calculations. The break condition for the self-consistent field (SCF) and ionic loops were set to $10^{-8}$ eV and $10^{-5}$ eV, $\text{Å}^{-1}$, respectively.

Total energies and Hellmann-Feynman forces were calculated for 26 structures resulting from individual displacements of the symmetry inequivalent atoms in the SC, along the six inequivalent Cartesian directions ($\pm x$, $\pm y$, and $\pm z$). Phonon density of states [39,40] and Raman frequencies were extracted from subsequent calculations using the direct method [53], as implemented in the PHONON software [54].

IV. RESULTS AND DISCUSSION

We performed temperature dependent INS measurements at 2, 30, 80, 160, and 300 K. The Bose-factor-corrected $S(Q, E)$ plots for Ba$_2$Ti$_2$Fe$_2$As$_4$O at 2 and 300 K, using different neutron incident energies, are shown in Fig. 2. The use of a higher incident energy allowed to explore a wider ($Q$, $E$) range, $Q_{\text{max}} \sim 10$ Å$^{-1}$. Whereas, a smaller incident energy ($E_i = 17$ meV) helped to explore a lower $Q$ range, down to $Q_{\text{min}} \sim 0.6$ Å$^{-1}$, relevant to magnetism, with a better energy resolution up to an energy transfer of 14 meV. Our measurements do not show any detectable magnetic signature in the attainable ($Q$, $E$) range of IN4C. There is an increase of the inelasticity as a function of temperature and $Q$, consistent with a phononlike behavior.

Phonon spectra, in terms of the generalized density of states [30,31], can be extracted using the $S(Q, E)$ function (cf. Sec. II). Figure 3 depicts the temperature dependence of the phonon spectra of Ba$_2$Ti$_2$Fe$_2$As$_4$O at 2, 30, 80, and 160 K. Our measurements show that the temperature variation has only a little effect on the evolution of the phonon spectra of Ba$_2$Ti$_2$Fe$_2$As$_4$O. Although this observation is quite similar to earlier studies on other Fe-based superconducting compounds (Refs. [36–38] and references therein), no conclusion could definitely be made on a possible unconventional behavior of Ba$_2$Ti$_2$Fe$_2$As$_4$O; dedicated theoretical treatments are clearly required—which is beyond the scope of the present paper.

The maximum attainable energy transfer on IN4C, offering an energy resolution reasonably enough to have a global view on the spanning of phonon modes, amounts to $\sim 50$ meV, using an incident neutron energy $E_i = 66$ meV ($\lambda_i = 1.11$ Å). This did not allow capturing the vibrational feature due to Ti-O stretching modes, which are expected to occur at higher frequencies, beyond the experimental energy window. A better energy resolution is ensured when using longer neutron incident wavelengths, at the price of reducing further the attainable energy transfer range (the measurements are performed in the neutron energy-loss mode). Phonon spectra collected using incident neutron energies $E_i = 39$ meV ($\lambda_i = 1.45$ Å) and $E_i = 17$ meV ($\lambda_i = 2.22$ Å) provide a better view on distinguishable phonon features, especially those lying in the low-frequency range. In order to have a full view on the phonon spectrum and to fulfill the aims abovementioned, as with respect to magnetism in Ba$_2$Ti$_2$Fe$_2$As$_4$O, we performed \textit{ab initio} DFT-based lattice dynamical calculations to accompany our INS measurements. Figure 4 compares our \textit{ab initio} calculated phonon spectra with the INS data at 2 and 300 K. As the measurements were performed using different incident neutron energies (wavelengths) to ensure a balance between phase space coverage and energy resolution, the calculated phonon spectrum was convolved with a Gaussian function (Fig. 4) with a specific width in order to mimic the instrumental resolution for each incident wavelength setting. The good agreement between the calculated phonon spectra and the measurements can be appreciated, in peak positions, intensities, and shapes.

FIG. 3. The temperature dependence of the phonon spectra GDOS of Ba$_2$Ti$_2$Fe$_2$As$_4$O using different incidence neutron wavelengths: 2.22 Å ($E_i = 17$ meV) (a), 1.45 Å ($E_i = 39$ meV) (b), and 1.11 Å ($E_i = 66$ meV) (c). Spectra are vertically shifted to help distinguishing the observed features.
specifically in the case of incident energy of 17 meV ($\lambda_i = 2.22 \text{ Å}$). Data collected using the shortest wavelength (1.11 Å) offers an extended energy range up to 50 meV, which is an instrumental limit in the used neutron energy loss setting, and the agreement with simulated spectra is not as good as in the case of $\lambda_i = 2.22 \text{ Å}$. Therefore, the validity and adequacy of the model calculation can be supported by considering the excellent agreement with the phonon spectra collected using a neutron incident wavelength of 2.22 Å ($E_i = 17$ meV), as well as with that taken at 1.45 Å ($E_i = 39$ meV).

The calculated phonon spectrum of Ba$_2$Ti$_2$Fe$_2$As$_4$O, as well as its partial atomistic, components are shown in Fig. 5. As abovementioned, the vibrational feature around 72 meV could not be captured in the present INS neutron energy-loss measurements. A closer look at the partial contributions allowed us to find that this feature is mainly due to O atoms, and to a much lesser extent to Ti, leading to Ti-O stretching modes (mass difference of Ti and O means that O exhibits a much stronger amplitude of motion). With the Ba atom as the heaviest one in Ba$_2$Ti$_2$Fe$_2$As$_4$O, its vibrational signature is mostly located at the low-frequency range around 8 and 10 meV. Ba$_2$Ti$_2$Fe$_2$As$_4$O includes two symmetry inequivalent sites occupied by As atoms. Their partial phonon densities of states reflect not only this nonequivalence, but also their bonding character in the crystal. Indeed, one Arsenide (As1) forms the [Fe$_2$As$_2$] layer, and this can be seen through the overlap of the partial densities of states of As1 and Fe, which span basically a frequency range up to 35 meV, whereas As2 exhibits a more localized density of states, mostly around 20 meV and seemingly decoupled from those of As1 and Fe. The localized behavior of As2 and Ba partial phonon densities of states points towards the ionic-like behavior of As2 and Ba, which is not implausible given that these two atom types are located between the layers and sheets formed by [FeAs$_1$] and [TiAsO], respectively.

Raman modes can also be extracted from our lattice dynamical calculations. Table I compares our calculated Raman frequencies of Ba$_2$Ti$_2$Fe$_2$As$_4$O from the presently used DFT-based direct method approach [53,54] and available experimental Raman data from Ref. [33] as well as other calculations based on linear response theory from the same work [33]. We notice the excellent agreement between the two types of lattice dynamical calculations and the observed values, which further validates our model calculation.

The simulated phonon spectra shown in Figs. 4 and 5, as well as our derived Raman frequencies gathered in Table I, were extracted from nonmagnetic (NM) lattice dynamical calculations performed on the experimentally refined structure. We have also performed other calculations [55,56] where possible effects of spin-polarization and/or electron correlation [32], via an on-site Hubbard-based correction [57,58], were considered. It comes out that only the presently reported phonon spectrum and Raman frequencies agree well with the measurements, reflecting therefore their correctness and the validity of the underlying model calculation. Indeed, including the spin polarization degree-of-freedom in the calculations based on the experimental structure [29], with or without taking into account electron correlation via DFT+$U$ procedure [57,58], resulted in a phonon spectrum showing
imaginary frequencies, signature of structural instabilities, or in the best case, a phonon spectrum and Raman frequencies not matching our INS measurements and available Raman data [33]. We also found that calculated phonon spectra and Raman frequencies using optimized geometries deviate from the observations, reflecting the sensitivity of phonon dynamics to subtle changes in the crystal structure [56].

Tables II and III gather structural parameters and estimated magnetic moments, respectively, from the different model calculations mentioned above. When neglecting the effect of electron correlation, the spin-polarization (SP) case relaxes to a NM structural solution (Table II), with a zero magnetic moment on both Ti and Fe sites (Opt in Table III). Expectedly, including explicitly on-site electron correlation [57] resulted in the emergence of magnetic moments on the Fe and Ti sites in both the optimized structure (OptHub) and the experimental structure (ExpHub). A similar case is found from calculations performed on the experimental structure with a noticeable difference in terms of a nonzero, but weak, magnetic moment on the Ti and Fe sites without considering electron correlation effect (Exp). We notice that the calculations provide two slightly different magnetic moments on the Ti site, which is of one crystallographic type.

The fact that only NM calculations, performed on the experimentally refined structure [29] reproducing the best our INS-based phonon spectra and Raman data [33] points towards a NM nature, or a very weak and complex magnetic interactions (if any) in Ba$_2$Ti$_2$Fe$_2$As$_4$O. Considering spin-polarization and/or on-site electron correlation seems to destabilize both the crystal and electronic structures [59]. Comparing to the experimentally refined structural parameters [29], the spin-polarized case, including the on-site electron correlation (Table II), resulted in overestimating the crystal volume by ~5 %, and an in-plane (ab) expansion of ~4 %, while the c axis is reduced by ~2.5 %. This might explain the structural instabilities reflected in the imaginary frequencies we mentioned above. From the analysis of the other model calculations we adopted, it seems that a correct description of the axial separation governing the interlayer interaction is very crucial in describing a coupled picture of both electronic and structural instabilities in Ba$_2$Ti$_2$Fe$_2$As$_4$O. Therefore, we speculate that this material might exhibit a charge DW (CDW) rather than a spin DW (SDW)-like character below T$_c$ = 125 K. This by no means is contradictory with the fact that non-negligible magnetic moments are found on Fe and Ti sites when on-site electron correlation correction is included in the calculations. Indeed, imposing an on-site Coulomb interaction reduces the metal (Fe, Ti)–ligand (O, As) hybridization and leads to a localized picture that could artificially raise magnetic moments on Fe and Ti site. This would not fully correspond to a metallic behavior of Ba$_2$Ti$_2$Fe$_2$As$_4$O [34,59].

In addition to our nonpolarized neutron INS measurements at IN4C, we performed polarized neutron diffraction measurements on DNS to attempt to get a clearer insight into the possible static magnetism in Ba$_2$Ti$_2$Fe$_2$As$_4$O. Figure 6 shows the difference of the nuclear (a) and magnetic (b) scattering components separated by $\chi_{ab}$-polarization analysis between 30 K (well below T$_c$) and 150 K (above T$_c$). The several dip-peak features in Fig. 6(a) arise from the shifting of the strong nuclear reflections while cooling. The net magnetic intensity at 30 K, after subtracting the background at 150 K, as shown in Fig. 6(b), is almost constant and close to zero, confirming the absence or extreme weakness of the magnetism blow T$_c$, if any, in Ba$_2$Ti$_2$Fe$_2$As$_4$O. This is well consistent with the conclusion drawn above that NM calculations can better reproduce the measured phonon spectra.

To summarize, our results point towards a NM character of the self-doping superconductor Ba$_2$Ti$_2$Fe$_2$As$_4$O, favoring a CDW instead of a SDW scenario as the origin of the transition

### Table I. Comparison of calculated and measured Raman shifts (cm$^{-1}$) of Ba$_2$Ti$_2$Fe$_2$As$_4$O.

|          | Eg(R) | A1g(R) | Eg(R) | A1g(R) | A1g(R) | B1g(R) | Eg(R) |
|----------|-------|--------|-------|--------|--------|--------|-------|
| Exp$^a$  | 61, 6 | 79, 9  | 114, 1| 147, 2 | 160, 6 | 194, 5 | 195, 6|
| Calc$^b$ | 62, 1 | 79, 7  | 135, 9| 146, 5 | 184, 6 | 199, 4 | 200, 7|
| Calc$^c$ | 62, 5 | 80, 9  | 129, 3| 148, 8 | 171, 6 | 196, 1 | 201, 6|

$^a$Experimental values taken from reference Ref. [33].
$^b$Calculated values based on linear response theory, taken from Ref. [33].
$^c$Present paper: calculated values based on the direct method approach (cf. Sec.III).

### Table II. Comparison of relaxed and experimentally refined structure parameters.

| a, b (Å) | c (Å) | V (Å$^3$) |
|----------|-------|-----------|
| Exp      | 4.0276| 27.3441   | 443.564 |
| NM or SP | 4.0360| 26.9884   | 439.622 |
| SP$^{Hub}$ | 4.1860| 26.6714   | 467.352 |
| NM$^{Hub}$ | 4.0758| 26.7161   | 443.812 |

### Table III. Estimated magnetic moments ($\mu_B$) per Ti and Fe site from our spin-polarized DFT-based calculations.

|       | Exp | Exp$^{Hub}$ | Opt | Opt$^{Hub}$ |
|-------|-----|-------------|-----|-------------|
| Ti    | 0.066, 0.035 | 0.8, 0.937 | 0.0 | 1.069, 1.239 |
| Fe    | 0.584 | 2.815      | 0.0 | 3.02        |
at \( T^* \). It is worth noting that no indications of a symmetry lowering expected for a SDW order were observed below \( T^* \) in \( \text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O} \) by Raman spectroscopy, supporting a CDW scenario as well [33]. In addition, although the CDW transitions are difficult to detect directly in most of the titanium oxypnictides, recent XRD and Raman scattering measurements were able to reveal the structural modulation associated with the CDW transition in \( \text{Na}_2\text{Ti}_2\text{As}_5\text{O} \) [60,61]. Further experiments on high-quality single crystals are desirable for providing direct evidences of the possible CDW order in \( \text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O} \).

**V. CONCLUSIONS**

Temperature-dependent INS measurements were performed on the self-doping superconducting material \( \text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O} \). No magnetic signature could be evidenced in the attainable \((Q, E)\) range of the experimental neutron energy loss setting. Phonon spectra were extracted from the INS measurements, and \textit{ab initio} lattice dynamical calculations were performed to accompany the measured spectra. Our determined phonon spectrum and Raman frequencies from \textit{ab initio} calculations agree well with our INS data and available Raman data [33]. Other calculations including spin-polarization and/or electron-correlation effects lead to phonon spectra deviating from the INS observations. This could be a signature of a destabilization of the crystal and electronic structures, in this case. Therefore, the NM framework describes the best the lattice dynamical behavior of \( \text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O} \), which could be a step further towards establishing a CDW character of this material, especially because no experimental evidence is available on any magnetic signature stemming from the Fe or Ti sites.

---

[1] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, \textit{J. Am. Chem. Soc.} \textbf{128}, 10012 (2006).
[2] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, \textit{J. Am. Chem. Soc.} \textbf{130}, 3296 (2008).
[3] A. J. Drew, Ch. Niedermayer, P. J. Baker, F. L. Pratt, S. J. Blundell, T. Lancaster, R. H. Liu, G. Wu, X. H. Chen, I. Watanabe, V. K. Malik, A. Dubroka, M. Rössle, K. W. Kim, C. Baines, and C. Bernhard, \textit{Nature Materials} \textbf{8}, 310 (2009).
[4] P. Dai, J. Hu, and E. Dagotto, \textit{Nature Physics} \textbf{8}, 709 (2012).
[5] G. R. Stewart, \textit{Rev. Mod. Phys.} \textbf{83}, 1589 (2011).
[6] H. Chen, Y. Ren, Y. Qiu, Wei Bao, R. H. Liu, G. Wu, T. Wu, Y. L. Xie, X. F. Wang, Q. Huang, and X. H. Chen, \textit{Europhys. Lett.} \textbf{85}, 17006 (2009).
[7] I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, \textit{Phys. Rev. Lett.} \textbf{101}, 057003 (2008).
[8] K. Kuroki, S. Onari, R. Arita, H. Usui, Y. Tanaka, H. Kontani, and H. Aoki, \textit{Phys. Rev. Lett.} \textbf{101}, 087004 (2008).
[9] A. D. Christianson, E. A. Goremychkin, R. Osborn, S. Rosenkranz, M. D. Lumsden, C. D. Malliakas, I. S. Todorov, H. Claus, D. Y. Chung, M. G. Kanatzidis, R. I. Bewley, and T. Guidi, \textit{Nature} \textbf{456}, 930 (2008).
[10] D. S. Inosov, J. T. Park, P. Bourges, D. L. Sun, Y. Sidis, A. Schneidewind, K. Hradil, D. Haug, C. T. Lin, B. Keimer, and V. Hinkov, \textit{Nature Phys.} \textbf{6}, 178 (2010).
[11] I. Eremin and A. V. Chubukov, \textit{Phys. Rev. B} \textbf{81}, 024511 (2010).
[12] T. Yildirim, \textit{Physica C} \textbf{469}, 425 (2009).
[13] L. Boeri, O. V. Dolgov, and A. A. Golubov, \textit{Physica C} \textbf{469}, 628 (2009).
[14] C. de la Cruz, W. Z. Hu, S. Li, Q. Huang, J. W. Lynn, M. A. Green, G. F. Chen, N. L. Wang, H. A. Mook, Q. Si, and P. Dai, \textit{Phys. Rev. Lett.} \textbf{104}, 017204 (2010).
[15] D. J. Singh and M. H. Du, \textit{Phys. Rev. Lett.} \textbf{100}, 237003 (2008).
[16] L. Boeri, O. V. Dolgov, and A. A. Golubov, \textit{Phys. Rev. Lett.} \textbf{101}, 026403 (2008).
[17] S. M. Shapiro, G. Shirane, and J. D. Axe, \textit{Phys. Rev. B} \textbf{12}, 4899 (1975).
[18] F. Weber and L. Pintschovius, \textit{Phys. Rev. B} \textbf{82}, 024509 (2010).
[19] J. D. Axe and G. Shirane, \textit{Phys. Rev. Lett.} \textbf{30}, 214 (1973).
[20] H. Kawano, H. Yoshizawa, H. Takeya, and K. Kadowaki, \textit{Phys. Rev. Lett.} \textbf{77}, 4628 (1996).
[21] F. Weber, A. Kreyssig, L. Pintschovius, R. Heid, W. Reichardt, D. Reznik, O. Stockert, and K. Hradil, \textit{Phys. Rev. Lett.} \textbf{101}, 237002 (2008).
[22] R. Osborn, E. A. Goremychkin, A. I. Kolesnikov, and D. G. Hinks, \textit{Phys. Rev. Lett.} \textbf{87}, 017005 (2001).
[23] F. Gompf, W. Reichardt, H. Schober, B. Renker, and M. Buchgeister, \textit{Phys. Rev. B} \textbf{55}, 9058 (1997).
[24] M. Rotter, M. Tegel, and D. Johrendt, \textit{Phys. Rev. Lett.} \textbf{101}, 077006 (2008).
[25] S. Matsuishi, Y. Inoue, T. Nomura, Y. Kamihara, M. Hirano, and H. Hosono, \textit{New J. Phys.} \textbf{11}, 025012 (2009).
[26] G. Wu, Y. L. Xie, H. Chen, M. Zhong, R. H. Liu, B. C. Shi, Q. J. Li, X. F. Wang, T. Wu, Y. J. Yan, J. J. Ying,
and X. H. Chen, J. Phys.: Condens. Matter 21, 142203 (2009). [27] M. S. Torikachvili, S. L. Budko, N. Ni, and P. C. Canfield, Phys. Rev. Lett. 101, 057006 (2008). [28] P. L. Alireza, Y. T. Chris Ko, J. Gillett, C. M. Petrone, J. M. Cole, G. G. Lonzarich, and S. E. Sebastian, J. Phys.: Condens. Matter 21, 012208 (2009). [29] Y. L. Sun, H. Jiang, H. F. Zhai, J. K. Bao, W. H. Jiao, Q. Tao, C. Y. Shen, Y. W. Zeng, Z. A. Xu, and G. H. Cao, J. Am. Chem. Soc. 134, 12893 (2012). [30] Y. L. Sun, A. Ablimit, J. K. Bao, H. Jiang, J. Zhou, and G. H. Cao, Sci. Technol. Adv. Mater. 14, 055008 (2013). [31] Y.-L. Sun, A. Ablimit, C.-M. Feng, and G.-H. Cao, J. Phys. Soc. Conf. Proc. 3, 015004 (2014). [32] J.-Z. Ma, A. van Roekeghem, P. Richard, Z.-H. Liu, H. Miao, L.-K. Zeng, N. Xu, M. Shi, C. Cao, J.-B. He, G.-F. Chen, Y.-L. Sun, G.-H. Cao, S.-C. Wang, S. Biermann, T. Qian, and H. Ding, Phys. Rev. Lett. 113, 266407 (2014). [33] S.-F. Wu, P. Richard, W.-L. Zhang, C.-S. Lian, Y.-L. Sun, G.-H. Cao, J.-T. Wang, and H. Ding, Phys. Rev. B 89, 134522 (2014). [34] H. P. Wang, Y.-L. Sun, X. B. Wang, Y. Huang, T. Dong, R. Y. Chen, G. H. Cao, and N. L. Wang, Phys. Rev. B 90, 144508 (2014). [35] Y. L. Sun, I. Felner, and G. H. Cao (private communication). [36] M. Zhiri, R. Mittal, S. Rols, Y. Su, Y. Xiao, H. Schober, S. L. Chaplot, M. Johnson, T. Chatterji, Y. Inoue, S. Matsuishi, H. Hosono, and Th. Brueckel, J. Phys.: Condens. Matter 22, 315701 (2010). [37] M. Zhiri, H. Schober, M. R. Johnson, S. Rols, R. Mittal, Y. Su, M. Rotter, and D. Johrendt, Phys. Rev. B 79, 064511 (2009). [38] R. Mittal, M. Zhiri, S. Rols, Y. Su, Y. Xiao, H. Schober, S. L. Chaplot, M. Johnson, T. Chatterji, S. Matsuishi, H. Hosono, and Th. Brueckel, Phys. Rev. B 79, 214514 (2009). [39] The lattice dynamical calculations provide the vibrational density of states (VDOS) [40], which should be transformed to the generalized density of states (GDOS) for a direct comparison with phonon spectra from inelastic neutron measurements. In contrast to VDOS, the GDOS (the phonon spectrum measured from INS) involves a weighting of the scatterers (ions) with their scattering powers \( \sigma/M \) (\( \sigma \): cross section; \( M \): mass). [40] S. N. Taraskin and S. R. Elliott, Phys. Rev. B 55, 117 (1997). [41] J. M. Carpenter and D. L. Price, Phys. Rev. Lett. 54, 441 (1985). [42] D. L. Price and K. Skold, in Neutron Scattering, edited by K. Skold and D. L. Price (Academic Press, Orlando, 1986), Vol. A. [43] A. J. Dianoux and G. Lander (eds.), Neutron Data Booklet (Institut Laue-Langevin, Grenoble, France, 2002). [44] Y. Su, K. Nemkovskiy, and S. Demirdis, J. Large-Scale Res. Facilities 1, A27 (2015). [45] O. Schärf and H. Capellmann, Phys. Stat. Sol. A 135, 359 (1993). [46] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999). [47] A. Dal Corso, Phys. Rev. B 82, 075116 (2010). [48] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964). [49] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965). [50] G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996). [51] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996). [52] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5187 (1976). [53] K. Parlinski, Z.-Q. Li, and Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997). [54] K. Parlinski, Software phonon (2003). [55] We performed several lattice dynamical calculations where possible effects of spin polarization and electron correlation were first considered, concomitantly or individually, then neglected to investigate their impact on phonon dynamics of \( \text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O} \). Phonon calculations were performed on both the experimentally refined structure as well as on relaxed geometries. Only the case of performing NM calculations on the experimental structure leads to a valid result as it is reflected by the excellent agreement with our INS work and Raman data [33,56]. [56] Calculated Raman frequencies in Ref. [33] were also extracted from NM lattice dynamical calculations using the experimentally refined crystal structure of \( \text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O} \). [57] Possible electron correlation effect was included in the calculation by using the on-site correction procedure DFT+U via the Dudarev approach [58]. We used values of the effective Coulomb (\( U \)) and exchange (\( J \)) parameters from Ref. [32]. The \( U \) parameter was set to 3.50 and 2.64 eV for Ti and Fe, respectively, while the \( J \) parameter was set to 0.74 and 0.96 eV for Ti and Fe, respectively. [58] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998). [59] It was not indicated in Ref. [32] whether the electron correlation based calculations included spin polarization effects. [60] D. Chen, T.-T. Zhang, Z.-D. Song, H. Li, W.-L. Zhang, T. Qian, J.-L. Luo, Y.-G. Shi, Z. Fang, P. Richard, and H. Ding, Phys. Rev. B 93, 140501 (R) (2016). [61] N. R. Davies, R. D. Johnson, A. J. Princep, L. A. Gannon, J.-Z. Ma, T. Qian, P. Richard, H. Li, M. Shi, H. Nowell, P. J. Baker, Y. G. Shi, H. Ding, J. Luo, Y. F. Guo, and A. T. Boothroyd, Phys. Rev. B 94, 104515 (2016).