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Terahertz pulse-driven collective mode in the nematic superconducting state of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ Romain Grasset^{1,2,3}✉, Kota Katsumi², Pierre Massat⁴, Hai-Hu Wen⁵, Xian-Hui Chen⁶✉, Yann Gallais^{1,2,4}✉ and Ryo Shimano^{1,2}✉

We investigate the collective mode response of the iron-based superconductor $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ using intense terahertz (THz) light. In the superconducting state a THz Kerr signal is observed and assigned to nonlinear THz coupling to superconducting degrees of freedom. The polarization dependence of the THz Kerr signal is remarkably sensitive to the coexistence of a nematic order. In the absence of nematic order the C_4 symmetric polarization dependence of the THz Kerr signal is consistent with a coupling to the Higgs amplitude mode of the superconducting condensate. In the coexisting nematic and superconducting state the signal becomes purely nematic with a vanishing C_4 symmetric component, signaling the emergence of a superconducting collective mode activated by nematicity.

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INTRODUCTION

Superconductivity with coexisting electronic orders can be found in various strongly correlated systems. Among these orders electron nematicity, where the electron fluid breaks the discrete rotational symmetry of the underlying lattice, has recently emerged as an ubiquitous phase in many superconductors ranging from cuprates¹, to iron-based superconductors² where superconductivity emerges within a nematic phase, and more recently doped Bi_2Se_3 ³ and twisted bi-layer graphene^{4,5} where the superconductivity itself may have a nematic component. In iron-based superconductors (Fe SC), superconductivity is found to coexist with both stripe-like magnetic spin-density-wave (SDW) and nematic orders. BaFe_2As_2 , a member of this family, undergoes a nematic-structural transition from a C_4 to a C_2 symmetric phase, followed by a SDW transition^{2,6}. The C_4 rotational symmetry breaking is triggered by electronic degrees of freedom and has been dubbed nematic for this reason^{2,7,8}. With increasing doping by substitution (e.g., Ba with K or Fe with Co^{6,9}), the C_2 symmetric nematic-SDW phase, hereafter called the C_2 phase, is weakened and a superconducting (SC) dome forms around a possible quantum critical point. The coexistence with the C_2 phase can profoundly impact the nature of SC order, by coupling different nearly degenerate pairing channels like s and d -wave^{10,11}, or inducing an orbitally-selective SC state^{12,13}.

One way to gain insight into the coupling between nematic and SC degrees of freedom is to study the collective modes of the SC state upon entering the C_2 SC phase. Theoretically, intertwined electronic orders where superconductivity coexists with other electronic orders can lead to a rich spectrum of SC collective modes^{14–24}. In a single band conventional superconductor the collective mode excitation spectrum consists of two modes: the Nambu-Goldstone phase mode which is shifted to the plasma frequency through the Anderson–Higgs mechanism, and the Higgs amplitude mode located at twice the SC gap energy. The Higgs mode does not couple linearly to light^{14,25,26}. Except in very special cases like charge-density-wave superconductors^{27–30},

its observation has remained elusive until very recently. In this context, strong terahertz (THz) pulses have emerged as a tool of choice because they can access hidden SC collective modes via nonlinear optical processes^{31–37}. This has led to the observation of the SC Higgs mode in several SC materials like NbN and Nb_3Sn , but also in cuprates and Fe SC^{38–45}. In the case of Fe SC however, little is known experimentally about the impact of nematicity on SC collective modes like the Higgs.

Here we investigate the THz nonlinear response of the Fe SC $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ where superconductivity coexists with a nematic order using a THz pump near-infrared (NIR) probe scheme. In the SC state, we observe an instantaneous response which follows the square of the THz electric field which is assigned to the nonlinear THz Kerr effect. In the absence of a coexisting nematic order the THz Kerr signal displays a C_4 symmetric polarization dependence consistent with a nonlinear coupling to the SC Higgs mode. In the presence of a coexisting nematic order, the THz Kerr signal displays a drastic change in its polarization dependence: from fully symmetric in the C_4 symmetric SC phase to fully nematic in the C_2 symmetric phase. We show theoretically that the onset of the THz Kerr Higgs response in the nematic channel can be qualitatively explained by taking into account the anisotropy of the electronic structure in the C_2 nematic phase. However, the complete disappearance of the C_4 symmetric signal in the C_2 SC phase cannot be captured within this simple picture, indicating a non-trivial interplay between the nematic and superconducting order parameters and the emergence of a collective mode, distinct from the Higgs mode. We tentatively assigned this mode to the Bardasis-Schrieffer (BS) mode connecting s -wave and d -wave superconducting ground states which become mixed in the C_2 symmetric SC phase.

RESULTS

Non-linear THz Kerr effect

We studied two single crystals of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ with $T_c = 26\text{K}$ (UD26) and $T_c = 37\text{K}$ (UD37). The UD26 crystal is slightly

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Fig. 1 Nonlinear THz response in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. **a** Sketch of the THz pump near-infrared (NIR) probe measurements. **b** Crystal structure of BaFe_2As_2 and the two polarization configurations used to determine the C_4 symmetric and nematic components of the transient reflectivity. Raman spectra of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ in the B_{1g} symmetry for UD37 (**c**) and UD26 (**d**) below T_c . 2Δ indicates superconducting gap from the hole pockets. The gray curve represents the energy spectrum of the THz pump. **e** For UD37, $\Delta R/R$ (blue line) along one of the Fe–Fe axis at 20 K ($T < T_c$) as a function of delay time between the pump and probe pulses. The instantaneous component that follows E_{pump}^2 (red line) component corresponds to the THz Kerr effect.

underdoped and exhibits a simultaneous nematic/SDW transition at $T_N \sim T_S \sim 90$ K. The UD37 crystal only exhibits a superconducting transition and is close to optimal doping. The terahertz-pump optical reflectivity probe (TPOP) measurement scheme is depicted in Fig. 1a. Measurements were carried out with a fixed THz pump polarization along the Fe–Fe direction but two different probe polarizations either parallel or perpendicular to the pump polarization (Fig. 1b). Fe–Fe directions are identified by a 45° tilt with respect to the edges of the crystals which are square-shaped.

In Fig. 1c, d, we compare the THz pump spectrum with the SC state Raman spectra of the two samples (See Supplementary Note 1 for more details). With an energy centered around $\omega_p = 0.6$ THz $= 20 \text{ cm}^{-1}$, the THz pump spectrum is located below the lowest superconducting gap $2\Delta_h$ observed by Raman scattering. Based on previous Raman and angle-resolved photoemission spectroscopy measurements this gap is assigned to the Γ centered hole pockets. The TPOP signal $\frac{\Delta R}{R}$ of UD37 below T_c is shown in Fig. 1e. It consists of essentially two components, an instantaneous component that follows the square of the THz electric field (E -field) (red line in Fig. 1e) and a broader decaying component which last several picoseconds after the pump pulse. In the following we will mostly focus on the instantaneous component, the THz Kerr effect, where the strong THz E -field modulates the optical reflectivity in the NIR regime⁴⁶. We note that in our measurements we only detect an instantaneous component that is proportional to the square of the THz E -field, consistent with the centrosymmetric crystal structure of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. No forbidden odd contribution is observed, as recently reported in the SC state of Nb_3Sn ⁴⁷ and attributed to THz field symmetry breaking.

The THz Kerr signal is described by a third-order nonlinear susceptibility $\chi^{(3)}(\omega; \omega, \Omega, -\Omega)$ ^{48,49}, where ω and Ω are the frequencies of the NIR pulse and THz-pump pulse, respectively. The THz pulse-induced reflectivity change $\Delta R/R$ can be expressed

in terms of $\chi^{(3)}$ (see Supplementary Note 3) as:

$$\frac{\Delta R}{R}(E_i^{\text{probe}}, E_j^{\text{probe}}) \sim \frac{1}{R} \frac{\delta R}{\delta \epsilon_1} \epsilon_0 [\text{Re} \chi_{ijkl}^{(3)}] E_k^{\text{pump}} E_l^{\text{pump}} \quad (1)$$

where E_i denotes the i th component of the THz-pump or probe E -field and ϵ_1 is the real part of the dielectric constant at 1.5 eV. The instantaneous Kerr signal of interest here implies $\Omega = 0$ in $\chi^{(3)}$. It is therefore independent of the pump frequency Ω and non-resonant^{42,49}. This is in contrast with the third-harmonic generation (THG) signal which is resonant when the pump frequency Ω equals the superconducting gap Δ ³¹.

In general, the onset of a THz Kerr signal below T_c can be assigned to two different processes: coupling to charge density fluctuations (CDF) like the one observed in Raman experiments, or to the SC Higgs mode. As previously shown in the case of NbN and cuprates important clues about the origin of the THz Kerr signal, and other third-order nonlinear effects like THG, can be obtained by investigating its polarization dependence^{32,35,36,40,42,43}.

Assuming C_4 tetragonal symmetry for the normal state of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, we can analyze the polarization dependence of $\chi^{(3)}(\theta_{\text{pump}}, \theta_{\text{probe}})$ in terms of the irreducible representations of D_{4h} point group as:

$$\chi^{(3)}(\theta_{\text{pump}}, \theta_{\text{probe}}) = \frac{1}{2} \left(\chi_{A_{1g}}^{(3)} + \chi_{B_{1g}}^{(3)} \cos 2\theta_{\text{pump}} \cos 2\theta_{\text{probe}} + \chi_{B_{2g}}^{(3)} \sin 2\theta_{\text{pump}} \sin 2\theta_{\text{probe}} \right) \quad (2)$$

where we have defined the symmetry-resolved nonlinear response functions: $\chi_{A_{1g}}^{(3)} = \chi_{aaaa}^{(3)} + \chi_{bbba}^{(3)}$, $\chi_{B_{1g}}^{(3)} = \chi_{aaaa}^{(3)} - \chi_{bbba}^{(3)}$ and $\chi_{B_{2g}}^{(3)} = \chi_{abab}^{(3)} + \chi_{abba}^{(3)}$, and $\theta_{\text{probe/pump}}$ are the angles between the probe/pump polarization vectors and the a axis of the one Fe unit cell. The A_{1g} is the fully symmetric representation and the B_{1g}/B_{2g} representation transform as $x^2 - y^2$ and xy , respectively.

Fig. 2 Temperature and symmetry dependence of the THz response. $\Delta R/R$ against the delay time in the C_4 symmetric (C_4) and nematic (Nem) channels at various temperatures for UD37 (a, b) and UD26 (c, d). Fitted curves for the different components of $\Delta R/R$ at $T < T_c$ for UD37 (e, g) and UD26 (f, h).

The B_{1g} representation has the same symmetry as the C_2 symmetric nematic order parameter found in Fe SC. For $\theta_{\text{pump}} = 0$, the A_{1g} and B_{1g} responses can be accessed using two distinct probe polarization orientations. Indeed making use of Eq. (1) we can write:

$$\begin{aligned} \frac{\Delta R}{R}^{C_4} &= \frac{\Delta R_a}{R_a} + \frac{\Delta R_b}{R_b} \propto \text{Re} \chi_{A_{1g}}^{(3)} \\ \frac{\Delta R}{R}^{\text{Nem}} &= \frac{\Delta R_a}{R_a} - \frac{\Delta R_b}{R_b} \propto \text{Re} \chi_{B_{1g}}^{(3)} \end{aligned} \quad (3)$$

where R_i ($i = a, b$) denotes the reflectivity for a probe polarization along the Fe–Fe axes (a, b) of Fig. 1b and for a fixed pump polarization along the a axis. Here, we have taken $R_a = R_b$ (C_4 tetragonal symmetry). Since the notations B_{1g} and A_{1g} are no longer valid in the C_2 symmetric orthorhombic phase, we will adopt the notation “ C_4 ” for C_4 symmetric and “nem” for nematic (or C_2 symmetric) when discussing the results below.

Response in the C_4 symmetric superconducting state

We start by discussing the C_4 symmetric and nematic components of the TPOP signal of the UD37 crystal for which only superconductivity is present. Figure 2a, b show the transient reflectivity obtained for both C_4 symmetric and nematic components in the UD37 crystal and at various temperatures ranging from 15 K to 70 K. The decaying part of the $\Delta R/R$ signal shows a strong increase in the C_4 symmetric channel across T_c indicating the superconducting transition (Inset of Fig. 3a). The instantaneous Kerr

component is only observed below T_c , confirming it is linked to the onset of superconductivity. On the other hand, in the nematic channel no significant changes appear in the transient reflectivity at all temperatures. Using the fitting procedure displayed in Fig. 2e, g, we can obtain the temperature dependencies of the instantaneous and decaying components of $\frac{\Delta R}{R}^{C_4}$ and $\frac{\Delta R}{R}^{\text{Nem}}$ (Fig. 3a). The decaying component displays a sharp extremum around T_c and is assigned to the dynamical relaxation of quasiparticles in the SC state (see Supplementary Note 2). The instantaneous component, attributed to the THz Kerr effect, shows a strong enhancement below T_c . The absence of the instantaneous Kerr component in the nematic channel argues in favor of a contribution arising from the Higgs excitation. Indeed, as shown in the case of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ cuprates CDF are expected to contribute to all symmetry channels whereas the Higgs contribution is only active in the fully symmetric, i.e., C_4 symmetric for a tetragonal crystal, channel^{35,36,40,42,50}. Interestingly, Raman scattering spectra on the same crystal in the SC state are dominated by the B_{1g} channel¹¹ (see Supplementary Fig. 1), indicating they mostly probe CDF contributions in stark contrast with the THz Kerr signal. We note that the respective weight between Higgs and CDF contributions to third-order nonlinear susceptibilities has been a subject of a debate since BCS calculations indicate dominant CDF contributions for a clean superconductor³². However, there is now an emerging consensus that disorder significantly boosts the Higgs contribution, thus giving a rationale to the dominance of the Higgs contribution

Fig. 3 | Instantaneous Kerr response. Temperature dependencies of the amplitude of the fitted instantaneous Kerr signals in the C_4 symmetric (C_4) and nematic (nem) channels for UD37 (a) and UD26 (b). Insets: Temperature dependencies of the amplitude of the fitted SC decaying signals. Calculated temperature dependence of Higgs contribution of the hole pockets to the instantaneous Kerr signals in the C_4 symmetric (C_4) and nematic (nem) channels for a tetragonal (c) and orthorhombic (d) symmetry of the electronic dispersion relation. The shape of the Fermi surfaces of our model is represented in blue and yellow. Inset: Ratio of the nematic and C_4 symmetric components of the Higgs response as a function of the nematic order parameter for the hole (blue) and electron pockets (red). Error bars are defined as the standard deviation.

observed in THz Kerr and THG experiments in all superconductors studied so far^{33,35,36,51,52}.

Response in the C_2 symmetric superconducting state

Having discussed the simple case of the C_4 symmetric superconductor case, let us now turn to the sample with a lower doping level, UD26 which display a C_2 symmetric SC phase with both nematic and SC orders. Figure 2c, d show the transient reflectivity obtained for both channels and at various temperatures ranging from 9.5 K to 110 K. Above T_c , in contrast to UD37, both C_4 symmetric and nematic components show a change in the transient reflectivity below $T_{S/N} \sim 90$ K indicating the transition to the C_2 symmetric nematic phase. The onset of a decaying signal in the nematic channel is consistent with optical pump optical probe measurements on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ which reported a similar strongly anisotropic signal below $T_{S/N}$ ⁵³. In principle, a mixture of C_2 domains of different orientation would average out the nematic component of our signal. The fact that we observe a significant non-zero $\frac{\Delta R}{R}^{\text{nem}}$ shows that one domain orientation prevails under our 250 μm laser spot. We attribute this relatively large domain size to residual strains on the sample due to sample mounting which act as symmetric breaking field and align the nematic domains.

Below T_c , an instantaneous Kerr component of $\Delta R/R$ that follows the squared THz-pump E-field is also identified, with however a striking difference compared to UD37. Indeed, while it is essentially absent in $\frac{\Delta R}{R}^{C_4}$, the instantaneous Kerr signal shows a strong enhancement below T_c in the $\frac{\Delta R}{R}^{\text{nem}}$ channel. Using the fitting procedure displayed in Fig. 2f, h, we obtained the amplitude of the instantaneous Kerr and decaying components

(see Fig. 3b and Supplementary Fig. 2). Interestingly, the channel dependencies of the instantaneous Kerr and decaying signal are distinct: while the instantaneous Kerr signal is fully nematic with no C_4 symmetric component within our experimental accuracy, the decaying signal is present in both channels with similar amplitudes at all temperatures.

Origin of the nematic response

The complete switch from C_4 symmetric to nematic channel of the instantaneous Kerr signal when going from the C_4 SC phase to the C_2 SC phase is the central finding of the present work. It indicates an unanticipated and profound impact of the C_4 symmetry breaking on the THz Kerr nonlinear optical signal of the SC state. We now explore different scenarios to explain this phenomena. First since the structural transition from tetragonal to orthorhombic involves a mixing of the A_{1g} and B_{1g} symmetry into the A_g symmetry, we naturally expect some mixing of the $\frac{\Delta R}{R}$ symmetry components due to the anisotropy of the optical constants. Based on optical measurements on detwinned BaFe_2As_2 samples⁵⁴ (see Supplementary Note 4), we determined quantitatively how the two symmetries are mixed from the calculation of the $\frac{1}{R} \frac{\partial R}{\partial \epsilon_1}$ prefactor in Eq. (1). We found at most a 25% anisotropy with respect to the a and b axes. As expected this anisotropy causes a non-zero nematic component. However, it leads to a $\frac{\Delta R}{R}^{\text{nem}}$ signal of at most 10% of the $\frac{\Delta R}{R}^{C_4}$ signal, and therefore plays a marginal role in the C_4 symmetric to nematic transition observed in the THz Kerr signal.

Having ruled out a simple effect of anisotropic linear optical constant, we are left with the properties of the nonlinear response $\chi^{(3)}$ itself. In the C_2 phase, the anisotropy of the electronic dispersion relation will also induce a non-zero component of the Higgs mode response in the nematic channel³⁷. We evaluated the activation of the Higgs response in the nematic channel by calculating the third-order nonlinear Higgs response (see Fig. 3c, d for the contribution of the hole pockets) using a three pocket model (2 hole-like and 1 electron-like) and an s-wave superconducting gap (see Supplementary Note 3 and 4). As expected, in the C_4 phase the Higgs response appears below T_c only in the C_4 symmetric channel in agreement with our observations in the UD37 sample. In the C_2 phase however, the distorted Fermi pockets due to finite nematic order parameter activate the Higgs mode in the nematic channel as observed experimentally. The activation grows with the nematic splitting energy Δ_{nem} but quickly saturates and decreases (see inset of Fig. 3d). We found that for any realistic nematic splitting energy and band parameters, the nematic response of either hole or electron pockets is at most 60% of the C_4 symmetric response, thus failing to explain the experimental observation. We note that a dominant contribution from CDF to the THz Kerr signal would be inconsistent with both the fully C_4 symmetric Kerr signal observed in UD37 and the fully nematic Kerr signal observed in UD26 (see Supplementary Note 5 for an evaluation of the CDF contribution).

DISCUSSION

From the above discussion, it appears that the strong dominance of the THz Kerr signal in the nematic channel of UD26 cannot be explained simply by the effect of the anisotropy of the optical constant or the electronic structure on the Higgs signal. We are thus left with more speculative scenarios. First, we discuss the possibility of an exotic SC order parameter in the C_2 phase. We note that an SC order parameter with lower symmetry like d -wave will not by itself activate a Higgs Kerr signal in non-fully symmetric channels as demonstrated in the case of cuprates^{37,42}, so that our observations cannot be easily linked to a change in SC gap symmetry at least for a single band superconductor. However, in multi-orbital systems like Fe SC it is possible that the internal

structure of Cooper pairs in orbital space profoundly affects the anisotropy of the Kerr Higgs signal. An intriguing possibility is the recent proposal of an orbital-selective SC state in the C_2 phase of FeSe¹³. Whether such state would by itself yield a Higgs signal in the nematic channel only is unclear and deserves further theoretical investigations.

Another possibility is that the THz Kerr signal arises from an SC collective mode which couples to the nematic order parameter. In $Ba_{1-x}K_xFe_2As_2$ s and d -wave pairing channels are close competitors, potentially giving rise to a BS mode in the nematic d wave channel^{10,55,56}. Several spectral features of the Raman spectrum of $Ba_{1-x}K_xFe_2As_2$ have indeed been interpreted as BS modes, consistent with theoretical evaluations of pairing instabilities in hole-doped $BaFe_2As_2$ ^{10,11,57,58} (see also Supplementary Note 1 for a discussion of the Raman spectra in the SC state). Recently, Muller et al. have argued that in the C_2 phase the BS mode will couple to the amplitude mode of the nematic order parameter, giving rise to a single coupled nematic-BS mode below the Higgs mode energy due to the appearance of a strongly mixed $s+d$ SC state²⁴. The stronger decaying signal in the UD26 sample compared to the UD37 sample well-below T_c supports the idea of an increased anisotropy of the SC gap in the C_2 SC phase in agreement with a significant d wave admixture. Interestingly, for parameters close to the critical point where the nematic phase terminates Muller et al. found that the coupled nematic-BS mode may become dominant over the Higgs mode in the short-time dynamics after a quench²⁴. Furthermore, we note that the BS mode has the nematic B_{1g} symmetry and will naturally give rise to a signal in the nematic channel⁵⁹. A computation of the third-order nonlinear susceptibility taking into account both s and d pairing channels in the presence of a finite nematic order parameter is desirable to further assess this scenario.

In conclusion, we have studied the impact of nematicity on the SC collective modes in $Ba_{1-x}K_xFe_2As_2$ via THz pump optical probe measurements. In the absence of nematicity we observe an instantaneous behavior of the optical reflectivity which we assign to a THz Kerr coupling to the Higgs mode. In the coexisting nematic + SC phase we observe a drastic change in the polarization dependence of the THz Kerr signal from purely C_4 symmetric to purely nematic. The change cannot be accounted by the anisotropy of the electronic properties and indicates the emergence of an SC collective mode which couples strongly to the nematic order parameter. The exact identification of this mode requires further investigation, but we suggest the BS mode connecting nearly degenerate s and d wave pairing ground states as a likely candidate.

METHODS

Samples

The two single crystals of $Ba_{1-x}K_xFe_2As_2$ with $T_c = 26$ K (UD26, $x \sim 0.23$) and $T_c = 37$ K (UD37, $x \sim 0.28$) were characterized by SQUID magnetometry, wavelength dispersing spectroscopy and Raman scattering measurements. The samples are square-shaped with sides of ~ 5 mm. The crystal orientations of both samples were confirmed by polarization-resolved Raman spectroscopy measurements.

Terahertz pump-optical reflectivity probe (TPOP)

Strong single cycle THz pump pulses (0.3–1 THz) with electric field reaching up to 350 kV/cm are generated using optical rectification of 1.5 eV NIR pulses in a LiNbO₃ crystal using the tilted pulse front technique^{60,61}. For optical probe measurements 100 fs duration NIR pulses at 1.5 eV are used with a fluence of 10–100 nJ/cm² and a spot size of 250 μ m in diameter. The repetition rate of the NIR laser is 1 kHz.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors (R.G., Y.G., and R.S.) upon reasonable request.

CODE AVAILABILITY

All the numerical codes that support the findings of this study are available from the corresponding authors (R.G., Y.G., and R.S.) upon reasonable request.

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AUTHOR CONTRIBUTIONS

The samples were grown by H.-H.W. and X.-H.C.; R.G. and K.K. performed THz pump optical probe experiments; P.M. performed Raman experiments; R.G. and Y.G. performed the calculations and analyzed data; Y.G. and R.S. supervised the project; all authors discussed the results and wrote the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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