Interplay of lattice, electronic, and spin degrees of freedom in detwinned BaFe$_2$As$_2$: A Raman scattering study
Phys. Rev. B 98, 075113 — Published 7 August 2018
DOI: 10.1103/PhysRevB.98.075113
Interplay of lattice, electronic and spin degrees of freedom in detwinned BaFe$_2$As$_2$: a Raman scattering study


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(Dated: July 18, 2018)

We report results of Raman scattering experiments on twin-free BaFe$_2$As$_2$ with the main focus placed on understanding the influence of electronic and spin degrees of freedom on the lattice dynamics. In particular, we scrutinize the $E_g$ modes and the As $A_{1g}$ mode. Each of the two $E_g$ phonons in the tetragonal phase is observed to split into a $B_{2g}$ and a $B_{3g}$ mode upon entering the orthorhombic stripe-magnetic phase. The splitting amounts to approximately 10 cm$^{-1}$ and less than 5 cm$^{-1}$ for the low- and the high-energy $E_g$ mode, respectively. The detailed study of the fully symmetric As mode using parallel incident and outgoing photon polarizations along either the antiferromagnetic or the ferromagnetic Fe-Fe direction reveals an anisotropic variation of the spectral weight with the energy of the exciting laser indicating a polarization-dependent resonance effect. Along with the experiments we present results from density functional theory calculations of the phonon eigenvectors, the dielectric function, and the Raman tensor elements. The comparison of theory and experiment indicates that (i) orbital-selective electronic correlations are crucial to understand the lattice dynamics and (ii) all phonon anomalies originate predominantly from the magnetic ordering and the corresponding reconstruction of the electronic bands at all energies.

PACS numbers: 63.20.K-, 78.30.-j, 74.70.Xa, 75.25.Dk

I. INTRODUCTION

One of the most debated issues in Fe-based superconductors is the interplay of spin, orbital and lattice degrees of freedom at the onset of magnetism, nematicity and superconductivity, particularly interplay between phonons and magnetic degrees of freedom. For instance, soon after the discovery of Fe-based superconductors the magnetic moment was predicted to couple to the As position. Zbiri et al. found a modulation of the electronic density of states at the Fermi energy $E_F$ by the two $E_g$ and the $A_{1g}$ modes. Various anomalies were observed experimentally using neutron, Raman and optical spectroscopy, but are not fully understood yet.

One particular effect is the observation of substantial Raman scattering intensity of the As phonon below the magneto-structural transition in crossed polarizations with the electric fields oriented along the axes of the pseudo-tetragonal 2 Fe unit cell [For the definition of the axes see Fig. 1 (a)]. From the weak coupling point of view it has been argued that the formation of a spin-density wave modifies the low-energy electronic structure near the Fermi level, and this modification leads to the anomalous intensity. On the other hand, recent experiments were interpreted by introducing a phenomenological coupling between the phonon and the particle-hole continuum scaling with the amplitude of ordered magnetic moment being on the order of 1 $\mu_B$. This approach is clearly beyond the weak-coupling regime. Density functional (DFT) calculations and general considerations suggest that substantial modifications of the electronic structure occur in a broad energy range of order $J_{\text{Rund}} \gtrsim$ 1 eV, corresponding to the Raman photon (as opposed to phonon) energy scale. This raises suspicion that a quantitative description of the modifications in the Raman spectra upon magnetic ordering should take into account the broad energy range covering the entire $d$–electron band widths. Unfortunately, previous studies were done either in twinned samples or using only a single excitation energy, which limited the scope of experimental data being, as a result, not sufficiently restrictive to different, maybe even contradictory, interpretations.

In this work we systematically address this issue experimentally, using untwinned samples and resonant Raman scattering, and interpret the results quantitatively, not on a phenomenological or model level, but using DFT calculations. Our two most vital conclusions are that (i) magnetism affects all Fe bands in an essential way and that has to be accounted for in explaining Raman efficiencies. (ii) The fact that Fe $d$ states are correlated on
a moderate, but considerable level, while As \( p \) states are not, is not just quantitatively, but qualitatively important in understanding the resonant behavior.

A key issue hindering straightforward DFT calculations is the fact that the high-temperature tetragonal phase is paramagnetically disordered, and cannot be simulated by calculations with suppressed local magnetism.\(^{18}\) As explained in detail below, we circumvented this problem by assuming a magnetic order that preserves the large (albeit probably still somewhat underestimated) magnetic moment but respects the tetragonal symmetry. Yet another issue was to account for the correlation-driven renormalization of the \( d \)-band width. To this end, we separated the energy bands into two windows, a high-energy one dominated by As and a low-energy one derived predominantly from Fe. The Fe states were then uniformly renormalized. With these two assumptions we could reproduce (i) the positions of the Raman-active phonons and their splitting and evolution in the detwinned orthorhombic antiferromagnetic state and (ii) Raman intensities, including the \( \tilde{a} \simeq \tilde{b} \) anisotropy as well as the complex resonant evolution with the laser light energy \( \hbar \omega_1 \). While it is not clear \textit{a priori} that the two computational tricks described above are sufficiently accurate, even being physically motivated, the results provide an experimental justification and convincingly substantiate the underlying physical concepts: the pivotal role of local moments in the lattice dynamics of Fe-based superconductors, and the importance of band renormalizations for \( d \)-electrons. This said, further calculations avoiding these approximations, such as full-scale DMFT computations, are quite desirable but are beyond the scope of this work.

II. METHODS

A. Samples

The BaFe\(_2\)As\(_2\) crystal was prepared using a self-flux technique. Details of the crystal growth and characterization are described elsewhere.\(^{19}\) BaFe\(_2\)As\(_2\) is a parent compound of double-layer iron-based superconductors and orders in a stripe-like spin density wave (SDW) below \( T_{\text{SDW}} \approx 135 \) K. Superconductivity can be obtained by substituting any of the ions or by pressure.\(^{20}\) In Ba(Fe\(_1-x\)Co\(_x\))\(_2\)As\(_2\) (0 < \( x \) \( \lesssim \) 0.06) the SDW is preceded by a structural phase transition from a tetragonal \( (I4/mmm) \) to an orthorhombic \( (Fmmm) \) lattice at \( T_s > T_{\text{SDW}} \).\(^{19}\) It remains a matter of debate as to whether or not \( T_{\text{SDW}} \) and \( T_s \) coincide in BaFe\(_2\)As\(_2\).\(^{19,21}\)

Fig. 1(a) shows the relation of the various axes. The axes of the tetragonal crystal (\( T > T_s \), green lines) are denoted \( a \) and \( b \) with \( a = b \). The axes of the magnetically ordered structure (4 Fe per unit cell, black lines), \( \tilde{a} \) and \( \tilde{b} \), differ by approximately 0.7% below \( T_{\text{SDW}} \)\(^{22}\) and the Fe-Fe distance along the \( \tilde{b} \) axis becomes shorter than along the \( \tilde{a} \) axis as sketched in Figure 1(a). As a result, the angle between \( a \) and \( b \) differs from 90° by approximately 0.4°.

Below \( T_{\text{SDW}} \) the spins order ferromagnetically along \( \tilde{b} \) and antiferromagnetically along \( \tilde{a} \). Due to the small difference between \( \tilde{a} \) and \( \tilde{b} \) the crystals are twinned below \( T_s \), and the orthogonal \( \tilde{a} \) and \( \tilde{b} \) axes change roles at twin boundaries running along the directions of the tetragonal \( a \) and \( b \) axes. The orthorhombic distortion makes the proper definition of the axes important as has been shown for twin-free crystals by longitudinal and optical transport as well as by ARPES.\(^{23-28}\) In order to obtain a single-domain orthorhombic crystal we constructed a
sample holder for applying uniaxial pressure parallel to the Fe-Fe direction.

B. Detwinning clamp

The detwinning clamp is similar to that used by Chu et al. Fig. 1(b) and (c) show, respectively, a schematic drawing and a photograph of the clamp. The sample is attached to a thermally sunked copper block (1) with GE varnish, which remains sufficiently elastic at low temperatures and maintains good thermal contact between the holder (3) and the sample (4). The stress is applied using a copper-beryllium cantilever (2) which presses the sample against the body of the clamp. Upon tightening the screws (5) the force on the sample can be adjusted. In our experiment, the pressure is applied along the Fe-Fe bonds. The c axis of the sample is perpendicular to the force and parallel to the optical axis. The uniaxial pressure can be estimated from the rate of change of the tetragonal-to-orthorhombic phase transition at \( T_s \). Using the experimentally derived rate of 11 K per 7 MPa we find approximately 35 MPa for our experiment to be sufficient to detwin the sample.

C. Light scattering

The experiment was performed with a standard light scattering setup. We used two ion lasers (Ar\(^+\) Coherent Innova 304C and Kr\(^+\) Coherent Innova 400) and two diode pumped solid state lasers (Coherent Genesis MX SLM, Laser Quantum Ignis) providing a total of 14 lines ranging from 407 nm to 676 nm, corresponding to incident energies \( \hbar \omega_1 \) between 3.1 and 1.8 eV. Due to this wide range the raw data have to be corrected. The quantity of interest is the response function \( R \chi^z(\Omega) \) where \( \Omega = \omega_1 - \omega_2 \) is the Raman shift, \( \omega_2 \) is the energy of the scattered photons and \( R \) is an experimental constant. Details of the calibration are described in Appendix A.

Application of the Raman selection rules requires well-defined polarizations for the exciting and scattered photons. The polarizations are given in Porto notation with the first and the second symbol indicating the directions of the incoming and scattered photons’ electric fields \( e_1 \) and \( e_5 \), respectively. We use \( xyz \) for the laboratory system [see Fig. 1(d)]. The \( xx \) plane is vertical and defines the plane of incidence, \( yz \) is horizontal, \( xy \) is the sample surface, and the \( z \) axis is parallel to the optical axis and to the crystallographic \( c \) axis. For the sample orientation used here (see Fig. 1) the Fe-Fe bonds are parallel to \( x \) and \( y \), specifically \( \vec{a} = (1, 0, 0) \parallel x \) and \( b = (0, 1, 0) \parallel y \). Since the orthorhombicity below \( T_s \) is small the angle between \( a \) and \( \vec{a} \) deviates only by 0.2° from 45°. It is therefore an excellent approximation to use \( a \parallel x' = 1/\sqrt{2}(x + y) \equiv 1/\sqrt{2}(1, 1, 0) \) and \( b \parallel y' = 1/\sqrt{2}(y - x) \equiv 1/\sqrt{2}(1, 1, 0) \).

D. Theoretical Calculations

The phonon eigenvectors \( Q^{(\nu)} \) (displacement patterns of the vibrating atoms in the branch \( \nu \)) and the energies of all Raman-active phonons of BaFe\(_2\)As\(_2\) in the tetragonal (I4/mmm) and the orthorhombic (Fmmm) phases were obtained from \textit{ab initio} DFT calculations within the Perdew-Burke-Ernzerhof parameterization\(^{31}\) of the generalized gradient approximation. The phonon frequencies were calculated by diagonalizing the dynamical matrices using the phonopy package.\(^{32,33}\) The dynamical matrices were constructed from the force constants determined from the finite displacements in \( 2 \times 2 \times 1 \) supercells.\(^{34}\) We used the projector augmented wave approximation,\(^{35}\) as implemented in the Vienna package (VASP).\(^{36–38}\) The Brillouin zone for one unit cell was sampled with a \( 10 \times 10 \times 10 \) \( k \) point mesh, and the plane wave cutoff was set at 520 eV. For the tetragonal phase, we used a Néel-type magnetic order to relax the structure and to obtain the experimental lattice parameters.\(^{39}\) For the orthorhombic phase, we used the stripe-like magnetic order shown in Fig. 1(a).
Table I. Raman-active phonons in BaFe$_2$As$_2$. The experimental and theoretically determined energies are given in cm$^{-1}$. In addition, the symmetry correlations between the tetragonal ($I4/mmm$) and orthorhombic ($Fmmm$) structures are shown.

<table>
<thead>
<tr>
<th>$I4/mmm$</th>
<th>$Fmmm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. (140 K) Theory</td>
<td>Exp. (60 K) Theory</td>
</tr>
<tr>
<td>$A_{1g}$</td>
<td>180</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>215</td>
</tr>
<tr>
<td>$E_{g}^{(1)}$</td>
<td>130</td>
</tr>
<tr>
<td>$E_{g}^{(2)}$</td>
<td>268</td>
</tr>
</tbody>
</table>

We have then calculated the complex Raman tensor $\alpha_{jk}^{(\nu)}(\omega_l) = \alpha_{jk}^{(\nu)'}(\omega_l) + i\alpha_{jk}^{(\nu)''}(\omega_l)$, defined as the derivative of the dielectric tensor elements $\varepsilon_{jk}(\omega_l) = \varepsilon_{jk}^{(\nu)'}(\omega_l) + i\varepsilon_{jk}^{(\nu)''}(\omega_l)$ with respect to the normal coordinate of the respective phonon, $Q^{(\nu)}$. Since we are interested only in the resonance behavior of the As phonons, we only needed the derivatives with respect to $Q^{(\nu)}(\text{As})$,

$$\alpha_{ll}^{(\text{As})}(\omega_l) = \frac{\partial \varepsilon_{ll}^{(\nu)'}(\omega_l)}{\partial Q^{(\nu)}(\text{As})} + i \frac{\partial \varepsilon_{ll}^{(\nu)''}(\omega_l)}{\partial Q^{(\nu)}(\text{As})}.$$

In order to calculate the dielectric (tensor) function $\varepsilon$ we used the optics code package$^{40}$ implemented in WIEN2k (Ref. 41) with the full-potential linearized augmented plane-wave (LAPW) basis. The Perdew-Burke-Ernzerhof generalized gradient approximation$^{41}$ was employed as the exchange correlation functional and the basis-size controlling parameter $R_{\text{Kmax}}$ was set to 8.5. A mesh of 400 k points in the first Brillouin zone for the self-consistency cycle was used. The density of states (DOS) and dielectric tensors were computed using a 10$\times$10$\times$10 k mesh. For the dielectric tensor a Lorentzian broadening of 0.1 eV was introduced.

### III. RESULTS AND DISCUSSION

#### A. Lattice dynamics

The energies and symmetries as obtained from lattice dynamical calculations for tetragonal and orthorhombic BaFe$_2$As$_2$ are compiled in Table I. The four modes in tetragonal $I4/mmm$ symmetry obey $A_{1g} + B_{1g} + 2E_{g}$ selection rules. The eigenvectors are depicted in Fig. 2. In the orthorhombic $Fmmm$ phase, the two $E_{g}$ modes are expected to split into $B_{2g}$ and $B_{3g}$ modes. Thus, there are six non-degenerate modes in the orthorhombic phase, $A_{g} + B_{1g} + 2B_{2g} + 2B_{3g}$. Table I shows the symmetry relations between the tetragonal and orthorhombic phonons.

Since the $A_{g}$ and $B_{1g}$ eigenvectors remain unchanged upon entering the orthorhombic phase, only those of the $B_{2g}$ and $B_{3g}$ phonons are shown in Fig. 3. For the $B_{2g}$ and $B_{3g}$ phonons the As and Fe atoms move perpendicular to the $c$ axis and perpendicular to each other. The calculated phonon vibrations agree with previous results for BaFe$_2$As$_2$,$^{7}$ however our energies differ slightly from those reported by Zbiri et al.$^{7}$ In particular, we find a splitting between the $B_{2g}^{(1)}$ and $B_{3g}^{(1)}$ phonons.
B. \( E_g \) phonons

Table I displays the experimental phonon energies above and below the magneto-structural transition, along with the theoretical values. The \( E_g^{(1)} \) phonon found at 130 cm\(^{-1}\) above \( T_s \) splits into two well separated lines as predicted (Table I) and shown in Fig. 4. The splitting of the \( E_g^{(2)} \) mode at 268 cm\(^{-1}\) is small, and the \( B_{2g}^{(2)} \) and \( B_{3g}^{(2)} \) modes are shifted to higher energies by 2 cm\(^{-1}\), and 5 cm\(^{-1}\), respectively.

The theoretical and experimental phonon energies are in agreement to within 14\% for both crystal symmetries. The splitting between the \( B_{2g} \) and \( B_{3g} \) modes is overestimated in the calculations.

Previous experiments were performed on twinned crystals,\(^8,42,43\) and the \( B_{2g} \) and \( B_{3g} \) modes were observed next to each other in a single spectrum. An equivalent result can be obtained in de- twinned samples by using \( x^{*}y \), \( x^{*}x \) or \( RR \) polarizations where the \( x \) and \( y \) axes are simultaneously projected (along with the \( z \) axis). In neither case the symmetry of the \( B_{2g} \) and \( B_{3g} \) phonons can be pinned down. Only in a de-twinned sample where the \( xz \) and \( yz \) configurations are projected separately the \( B_{2g} \) and \( B_{3g} \) modes can be accessed independently.

Uniaxial pressure along the Fe-Fe direction, as shown by the black arrows in the insets of Fig. 4, determines the orientation of the shorter \( \hat{b} \) axis. This configuration enables us to observe the \( B_{2g}^{(1)} \) mode at 125 cm\(^{-1}\) and the \( B_{3g}^{(1)} \) mode at 135 cm\(^{-1}\) in \( x^{*}x \) and, respectively, \( x^{*}y \) polarization configurations thus augmenting earlier work. With the shorter axis determined by the direction of the stress (insets of Fig. 4) the assignment of the \( B_{2g} \) and \( B_{3g} \) modes is unambiguous. Since the \( x^{*}x \) spectrum (red) comprises \( a\hat{a} \) and \( c\hat{a} \) polarizations both the \( A_g \) and the \( B_{2g} \) phonons appear. The \( x^{*}y \) spectrum (blue) includes the \( B_{1g} \) (\( \hat{a}\hat{b} \)) and \( B_{3g} \) (\( \hat{c}\hat{b} \)) symmetries.

The calculated splitting between the \( B_{2g} \) and \( B_{3g} \) modes is smaller for the \( E_g^{(2)} \) than for the \( E_g^{(1)} \) mode, qualitatively agreeing with the experiment. However, in the calculations this difference is entirely due to the different reduced masses for these modes since the \( E_g^{(1)} \) and \( E_g^{(2)} \) phonon are dominated by As and Fe motions, respectively. In the experiment the splitting for the \( E_g^{(2)} \) mode is close to the spectral resolution, indicating an additional reduction of the splitting below that obtained in the calculation. The source of this additional reduction is unclear at the moment.

C. As phonon line intensity

Fig. 5 shows low-energy spectra of twinned BaFe\(_2\)As\(_2\) for (a) \( RR \) and (b) \( ab \) polarization configurations at 310 (orange), 150 (green), and 60 K (blue). The As phonon at 180 cm\(^{-1}\) is the strongest line in the \( RR \) spectra at all temperatures as expected and gains intensity upon cooling. In \( ab \) polarizations there is no contribution from the As mode above \( T_s \). Below \( T_s \) (blue spectrum) the As phonon assumes a similar intensity as in the \( RR \) polarization as reported earlier.\(^6,17\) Due to a finite projection of the incident light polarizations onto the \( c \) axis [see Fig. 1(d)] in both \( RR \) and \( ab \) configurations the \( E_g \) phonon appears in all spectra (asterisks). The electronic continuum has been extensively discussed in previous works\(^44-48\) and is not a subject of the study here.

In order to understand the appearance of the As line in the crossed \( ab \) polarizations it is sufficient to consider the in-plane components of the \( A_g \) Raman tensor,

\[
\hat{a}^{(Ag)} = \left( \begin{array}{cc} \alpha_{11} & 0 \\ 0 & \alpha_{22} \end{array} \right). \tag{2}
\]

The response of this phonon for the polarization configuration \( (e_i,e_S) \) is given by \( \chi_{1S}^{(Ag)} \propto |e_S^* \cdot \hat{a}^{(Ag)} \cdot e_i|^2 \) (where * means conjugate transposed). In the tetragonal \( (A_{1g}) \) case the two elements are equal, \( \alpha_{11} = \alpha_{22} \), and the phonon appears only for \( e_S \parallel e_i \). In the orthorhombic phase the tensor elements are different, and one can expect the phonon to appear for \( e_S \perp e_i \) since the intensity then depends on the difference between \( \alpha_{11} \) and \( \alpha_{22} \).

In detwinned samples \( \alpha_{11} \) and \( \alpha_{22} \) can be accessed independently by using parallel polarizations for the incident and scattered light oriented along either the \( \hat{a} \) or the \( \hat{b} \) axis. In addition, putative imaginary parts of \( \alpha_{ii} \) may be detected by analyzing more than two polarization combinations as discussed in Appendix C. Spectra for \( \hat{a}\hat{a} \) and \( \hat{b}\hat{b} \) configurations are shown in Figure 7 of Appendix B and we proceed here directly with the analysis of the phonon spectral weight \( A_{1S}^{(A_S)}(\omega_1) \) as a function of the incident photon excitation energy \( (\hbar\omega_1) \) and polarization.
Fig. 6(a) shows $A_{\tilde{a}\tilde{a}}^{(As)}(\omega)$ as derived by fitting the peak with a Voigt function, after subtracting a linear background. Measurements were repeated several times in order to check the reproducibility. The variation of the spectral weight between different measurements can be taken as an estimate of the experimental error. For light polarizations parallel to the antiferromagnetic $\tilde{a}$ axis, $A_{\tilde{a}\tilde{a}}^{(As)}(\omega)$ (red squares) increases continuously with increasing $h\omega$ whereas $A_{\tilde{b}\tilde{b}}^{(As)}$ (blue squares) stays virtually constant for incident photons in the red and green spectral range, $h\omega < 2.7$ eV, and increases rapidly for $h\omega > 2.7$ eV. For all wavelengths the spectral weight is higher for the $\tilde{a}\tilde{a}$ than for the $\tilde{b}\tilde{b}$ configuration.

The variations of $A_{\tilde{a}\tilde{a}}^{(As)}(\omega)$ and $A_{\tilde{b}\tilde{b}}^{(As)}(\omega)$ display a typical resonance behavior, which is expected when the intermediate state of the Raman scattering process is an eigenstate of the electronic system. Then, in second order perturbation theory, the intensity diverges as $|\hbar\omega - E_0|^2$ where $E_0$ is the energy difference between an occupied and an unoccupied electronic Bloch state. In real systems having a finite electronic lifetime a Lorentzian profile is expected. We therefore approximated $A_{\tilde{a}\tilde{a}}^{(As)}(\omega)$ with Lorentzians centered at $E_{0,\tilde{a}\tilde{a}}$ as shown by solid lines in Fig. 6(a). From these model functions we determine $E_{0,\tilde{a}\tilde{a}} = 3.1$ eV and $E_{0,\tilde{b}\tilde{b}} = 3.3$ eV.

As discussed in the Introduction, the band structure needs to be renormalized so as to account for correlation effects (for details see Appendix D). To this end, we differentiated three regions: (i) the unoccupied Fe $3d$ bands near the Fermi energy that we rescale uniformly, (ii) the occupied bands below -2.7 eV of predominantly As $4p$ character that remain unchanged and (iii) the occupied bands between -2.7 eV and the Fermi level derived from hybridized Fe $3d$ and As $4p$ orbitals. Due to this hybridization, the renormalization of the latter bands cannot be performed by simple rescaling. One can anticipate that the optical absorption would set in at energies below 1.8 eV, smaller than our minimal laser energy, if the occupied Fe bands would have been renormalized prior to hybridization with the As bands. Due to the small density of states of the As bands in the range from -2.7 eV to $E_F$ their contribution to the dielectric function would be small. With this in mind, we simply excluded all occupied bands in this range from the calculations. The effect of these bands, although small, could be accounted for using the DMFT method, which, however, is beyond the scope of our present work.

The results obtained as described above are presented in Fig. 6(b). One can see that the resonances lie in the range $h\omega > 2.7$ eV, and our calculations capture both the intensities and the $\tilde{a} - \tilde{b}$ anisotropy in this range rather well. Note that the antiferromagnetic ordering along the $\tilde{a}$ axis entails a backfolding of the electronic bands; we tentatively ascribe the much larger width of the resonance in the $\tilde{a}\tilde{a}$ configuration to this backfolding.

A corollary of our analysis is that resonance effects are the main source of the anomalous intensity of the As phonon in crossed polarizations. The main experimental argument is based on the anisotropic variation of the phonon intensities with $h\omega$ in $\tilde{a}\tilde{a}$ and $\tilde{b}\tilde{b}$ polarization configurations that comes about because of band reconstruction at higher energies. As proposed previously, magnetism appears to be the origin of the anisotropy. However, the intensity anisotropy cannot be explained without taking into account the high-energy electronic states.

Finally, we briefly look into the cross-polarization anomaly and find further support for its magnetic origin. In Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ the transition temperature $T_{SDW}$ is several degrees below $T_c$ for a finite $x$, and one observes that the anomaly of the As phonon does not appear at $T_c$, but rather at the magnetic transition.
$x = 0.025$ the phonon assumes intensity in crossed polarizations only below $T_{SDW}$ (see supplementary information of Ref. 47). For $x = 0.051$ the anomaly appears at $T_s$, as displayed in Fig. 10 in the Appendix but the spectral weight does not show an order-parameter-like temperature dependence. The increase is nearly linear and saturates below $T_{SDW}$ at a value which is smaller by approximately a factor of 7 than that in the $RR$ polarization projecting $A_g/A_g$ symmetry. In FeSe, with a structural transition at $T_s = 89.1$ K but no long range magnetism, the anomalous intensity can also be observed below $T_s$ but the intensity relative to that in the $A_g$ projection is only 1%, as shown in Fig. 11. Similar to Ba(Fe$_{0.94}$Co$_{0.051}$)$_2$As$_2$, the spectral weight increases approximately linearly but does not saturate, presumably because FeSe does not develop a long-ranged magnetic order.

**IV. CONCLUSION**

We studied the Raman scattering for three As phonons, the two $E_g$ and the one fully symmetric modes, in twin-free BaFe$_2$As$_2$, accompanied by DFT calculations of Raman intensities, with the goal of clarifying the impact of magnetism on electrons and phonons.

The tetragonal $E_g$ phonons at $130$ cm$^{-1}$ ($E_g^{(1)}$) and $268$ cm$^{-1}$ ($E_g^{(2)}$) were studied with the laser line at 532 nm and found to split into two modes in the orthorhombic phase. The detwining allows us to identify the modes at $125$ cm$^{-1}$ and $135$ cm$^{-1}$ as the $B_{2g}^{(1)}$ and $B_{3g}^{(1)}$ phonons, respectively. DFT calculations predict the symmetries correctly and show that the splitting occurs because of the stripe magnetic order (and not because of the orthorhombic distortion).

The As $A_g$ phonon was studied for various laser lines in the range 1.8 to 3.1 eV. In the ordered phase the spectral weight of the phonon resonates for an excitation energy of (3.2±0.1) eV. The resonance energy is almost the same for the light polarized along the ferro- or antiferromagnetic directions $\hat{b}$ and $\hat{a}$ [for the definition of the axes see Fig. 1(a)], whereas the variation of the spectral weight with the energy of the incident photon is rather different for the $\hat{b}\hat{b}$ and $\hat{a}\hat{a}$ configurations. The larger width of the resonance in $\hat{a}\hat{a}$ configuration can be understood qualitatively in terms of band backfolding along the antiferromagnetic direction.

Our DFT calculations reproduce the anisotropy and the resonance very well for energies above 2.7 eV if we include both the effects of the magnetism and of the correlations-induced renormalization of Fe 3$d$ bands. Due to DFT limitations, for energies below 2.7 eV, where correlated Fe 3$d$ bands are strongly hybridized with the As bands, our approximation is only semi-quantitative. Further studies based, for instance, on DMFT or other many-body methods are needed to test this approximation, apart from experimental verification. As in the case of the $E_g$ phonons, all effects are strongly linked to magnetism. However, in the case of the As phonon the inclusion of electronic states at high energies is essential because of the observed resonance behavior. Weak-coupling, low-energy physics with magnetism-induced anisotropic electron-phonon coupling appears insufficient for explaining the anomalous intensity in crossed polarizations.

More generally, our experimental observations and theoretical studies indicate the importance of orbital-dependent band renormalizations and of (nearly) localized ordered spins on the electronic properties at all energy scales.

**ACKNOWLEDGEMENT**

We gratefully acknowledge discussions with L. Degiorgi and thank him for providing us with raw and analyzed IR data of BaFe$_2$As$_2$. The work was supported by the Deutsche Forschungsgemeinschaft (DFG) via the Priority Program SPP 1458, the Transregional Collaborative Research Centers TRR 80, TRR 49 and by the Serbian Ministry of Education, Science and Technological Development under Project III45018. We acknowledge support by the DAAD through the bilateral project between Serbia and Germany (grant numbers 56267076 and 57142964). The collaboration with Stanford University was supported by the Bavaria California Technology Center BaCaTeC (grant-no. A5 [2012-2]). Work in the SIMES at Stanford University and SLAC was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Contract No. DE-AC02-76SF00515. Y.L. and R.V. acknowledge the allotment of computer time at the Centre for Scientific Computing (CSC) in Frankfurt. I.I.M. was supported by ONR through the NRL basic research program and by the Alexander von Humboldt foundation.
Appendix A: Calibration of the sensitivity

Scattering experiments performed over a wide energy range necessitate an appropriate correction of the data. The quantity of interest is the response function $R\chi''(\Omega)$ where $\Omega = \omega_1 - \omega_S$ is the Raman shift, and $\omega_S$ is the energy of the scattered photons. $R$ includes all experimental constants and units in a way that $R\chi''(\Omega)$ is as close as possible to the count rate $N_{IS}^s$, measured for a given laser power $P_l = I_l \hbar \omega_1$ absorbed by the sample. $I_l$ is the number of incoming photons per unit time and $I, S$ refer to both photon energies and polarizations. With $A_l$ the (nearly) energy-independent area of the laser focus the cross section is given by

$$\frac{N_{IS}^s(\Delta\omega_S, \Delta\Omega)}{P_l I_{01}} h\omega_1 A_l = R^* r(\omega_S) \frac{d^2\sigma}{d\omega_S d\Omega} \Delta\omega_S \Delta\Omega. \quad (A1)$$

Here, $r(\omega_S)$ is a constant and the relative sensitivity, respectively. $r(\omega_S)$ is assumed to be dimensionless and includes energy-dependent factors such as surface losses, penetration depth, and the monochromatic efficiency of the setup. $\Delta\omega_S$ and $\Delta\Omega$ are the bandwidth and the solid angle of acceptance, respectively, and depend both on $\omega_S$. $r(\omega_S) \Delta\omega_S \Delta\Omega$ is determined by calibration and used for correcting the raw data. The resulting rate $N_{IS}$ is close to $N_{IS}^s$ in the range $\Omega \leq 1,000$ cm$^{-1}$ but increasingly different for larger energy transfers mainly for the strong variation of $\Delta\omega_S$. Applying the fluctuation-dissipation theorem, one obtains

$$\frac{\dot{N}_{IS} h\omega_1 A_l}{P_l} = R' \frac{d^2\sigma}{d\omega_S d\Omega}$$

$$= R' \frac{h}{I_0} \frac{2\omega_S}{\omega_1} (1 + n(\Omega, T)) \chi''(\Omega), \quad (A2)$$

where $R'$ is another constant, which is proportional to $\Delta\omega_S(\omega_1) \Delta\Omega(\omega_1), n(\Omega, T) = [\exp(\frac{\hbar \Omega}{k_B T}) - 1]^{-1}$ is the thermal Bose factor and $I_0$ is the classical electron radius. Finally, after collecting all energy-independent factors in $R$ we obtain

$$R\chi''(\Omega) = \frac{\dot{N}_{IS} \omega_1^2}{P_l \omega_0^2} \frac{1}{\omega_0^2 \omega_1} \left[ 1 - \exp \left( -\frac{\hbar \Omega}{k_B T} \right) \right]. \quad (A3)$$

Here, $\omega_0 = 20,000$ cm$^{-1}$ is inserted for convenience to get a correction close to unity. Therefore, the spectra shown reflect the measured number of photon counts per second and mW absorbed power as closely as possible, thus approximately obeying counting statistics as intended. Since the spectra are taken with constant slit width the spectral resolution depends on energy, and narrow structures such as phonons may change their shapes but the spectral weight is energy independent.

Appendix B: $A_g$ spectra

Fig. 7 shows the complete set of the $A_g$ spectra we measured for detwinned Ba Fe$_2$As$_2$ and used for deriving the spectral weights $A_{aa}^{(As)}(\omega_1)$ and $A_{bb}^{(As)}(\omega_1)$ displayed in Fig. 6(a). All spectra were corrected as described in Appendix A. For all spectra the same constant width of 550 nm of the intermediate slit of the spectrometer was used. This results in an energy-dependent resolution varying between approximately 12 cm$^{-1}$ at 24,630 cm$^{-1}$ (3.05 eV or 406 nm) and 3 cm$^{-1}$ at 14,793 cm$^{-1}$ (1.83 eV or 676 nm). Accordingly, the width of the peak changes as a function of the excitation wavelength and does not reflect the intrinsic line width of the phonon, in particular not for blue photons. The intensity of the peak monotonically increases towards short wavelengths for the $A_a$ spectra (solid lines). For light polarized parallel to the ferromagnetic axis (\(b\bar{b}\), dashed lines) the intensity is low for $\lambda_l > 450$ nm, but strongly increases for $\lambda_l < 450$ nm. The underlying electronic continuum, which is not a subject of this paper, also changes in intensity as a function of the excitation wavelength. From the spectra the spectral weight $A_{ab}^{(As)}(\omega_1)$ of the phonon can be derived by fitting a Voigt function to the phonon peak after subtracting a linear background. The width of the Gaussian part of the Voigt function is given by the known resolution of the spectrometer while that of the Lorentzian part reflects the line width of the phonon.

Appendix C: Spectral weight for $aa$ and $ab$ polarizations

Since the ratio $A_{ab}^{(As)} / A_{aa}^{(As)}$ was not in the main focus of our work Fig. 6(a) displays only part of the data we collected. We also measured spectra in $aa$ and $ab$ configurations (cf. Figs. 1(a) and 8 for the definitions) and find them instructive for two reasons. The $aa$ and $ab$
The DFT band structure is shown in Fig. 9. Bands predominantly from Fe states are shown in brown, bands predominantly from As states in black. The shaded region from -2.7 eV to $E_F$ contains bands of mixed character and is blacked out for the calculation of the dielectric tensor. Only transitions between the bands within the turquoise frames are included.

**Appendix D: Band structure and PDOS**

The DFT band structure is shown in Fig. 9. Bands above $E_F$ stem predominantly from Fe 3$d$ orbitals (brown) while for $E < -2.7$ eV As 4$p$ orbitals prevail (black). For a suitable comparison to the experiment these Fe bands are renormalized by a factor between 2 and 3 (Refs. 54–57) while no renormalization is needed for the As bands. The bands between -2.7 eV and $E_F$ are of mixed Fe/As character and are left out when calculating the dielectric tensor as is illustrated by the grey shade in Fig. 9. Only transitions between the ranges
[-5.5 eV, -2.7 eV] and [0.2, 6 eV], highlighted by turquoise rectangles, are taken into account. Thus for photon energies below 2.7 eV the absorption in our calculations originates predominantly from the Drude response whereas for $\hbar \omega > 2.7$ eV the results become increasingly realistic since they include interband absorption. In either case we use a phenomenological damping of 0.1 eV. We determine the dielectric tensor and the Raman tensor as described in section II D on the basis of this renormalized band structure. While the $\hat{a} - \hat{b}$ anisotropy is qualitatively reproduced for all energies $\omega$ as shown in Fig. 6(b) of the main text, the two other experimental quantities, $A_{ii}^{(\alpha)}(\omega)$ (purple) and $A_{ia}^{(\alpha)}(\omega)$ (orange) shown in Fig. 8 here, are not captured properly simply because the imaginary parts of the theoretically determined tensor elements $\alpha_{ii}^{(\alpha)\prime\prime}$ become very small below 2.7 eV. In order to describe $A_{ia}^{(\alpha)}(\omega)$ and $A_{ia}^{(\alpha)}(\omega)$ absorption processes which lead to imaginary parts of the Raman tensor are necessary. Upon phenomenologically introducing imaginary parts of $\hat{a}$ for low energies, which cut off at 2.7 eV where the correct absorption takes over, full agreement can be achieved. However, a solution on a microscopic basis becomes possible only by using schemes that include many-body effects beyond DFT.

Appendix E: Interrelation of the $A_g$ phonon anomaly and magnetism in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and FeSe

![Figure 10](image-url) **Figure 10.** (Color online) As phonon in crossed polarizations for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ at $x = 0.051$. (a) Raw data for temperatures as indicated. The phonon position is shown as vertical dash-dotted line. The spectra are shifted vertically for clarity. (b) Temperature dependence of the spectral weight. The spectral weight in $A_g$ symmetry (orange circles) was multiplied by 0.15. $T_s$ and $T_{SDW}$ are indicated as vertical dashed lines.

Similarly as in BaFe$_2$As$_2$, the anomalous intensity of the $A_g$ phonon in crossed polarizations is linked to magnetic order also in other Fe-based systems as shown for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ at $x = 0.025$ a while ago and more recently for EuFe$_2$As$_2$, NaFeAs, LaFeAsO, and FeSe. Here, we add a few more results which support our interpretation. Fig. 10(a) shows Raman spectra in $ab$ polarization of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with $x = 5.1\%$ having $T_s = 60.9$ K and $T_{SDW} = 50.0$ K. The $A_g$ mode appears below $T_s$ and gains strength upon cooling. Fig. 10(b) shows the corresponding spectral weight as a function of temperature. In the nematic phase $T_{SDW} < T < T_s$ the phonon spectral weight increases almost linearly upon cooling (rather than order-parameter like), becomes constant in the magnetic phase for $T < T_{SDW}$ and reaches approximately 15% of that in the fully symmetric channel ($A_g/A_g$).

In FeSe the Se phonon appears also in the $ab$ spectra as shown in Fig. 11(a) when the temperature is lowered below the structural phase transition at $T_s \approx 90$ K. Upon cooling [Fig. 11(b)] the spectral weight of the phonon increases almost linearly for crossed polarizations (black squares), but stays virtually constant across the phase transition for parallel light polarizations (orange circles in Fig. 11(b)]. As opposed to Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ no saturation of the spectral weight in $ab$ polarizations is found, likely because FeSe shows no long range magnetic order down to the lowest temperatures. Only about 15% of the spectral weight of the $A_{1g}$ spectra (RR) is found in crossed polarizations here, in contrast to BaFe$_2$As$_2$ and Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ where the spectral weight of the phonon is larger (Figs. 5 and 10).

The nearly linear temperature dependence in both FeSe and Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and the larger saturation value in magnetically ordered Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ indicate that the anomalous intensity is more likely related...
to magnetism than to the orthorhombic distortion.
Ming Yi, Donghui Lu, Jiun-Haw Chu, James G. Anand, John P. Perdew, Kieron Burke, and Matthias Ernzerhof.


The local correlations in the tetragonal phase are of the stripe type; however, we had to use a pattern that does not break the symmetry, and it is known that the difference in the calculated elastic properties calculated within different magnetic orders is much smaller than between magnetic and nonmagnetic calculations.


