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Vibrational anomalies in $A\text{Fe}_2\text{As}_2$ ($A = \text{Ca}, \text{Sr}, \text{ and Ba}$) single crystals

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The detailed behavior of the in-plane infrared-active vibrational modes has been determined in $A\text{Fe}_2\text{As}_2$ ($A = \text{Ca}, \text{Sr}, \text{ and Ba}$) above and below the structural and magnetic transitions at $T_N = 172, 195$ and 138 K, respectively. Above T_N , two infrared-active E_u modes are observed. In all three compounds, below T_N the low-frequency E_u mode is observed to split into upper and lower branches; with the exception of the Ba material, the oscillator strength across the transition is conserved. In the Ca and Sr materials, the high-frequency E_u mode splits into an upper and a lower branch; however, the oscillator strengths are quite different. Surprisingly, in both the Sr and Ba materials, below T_N the upper branch appears to be either very weak or totally absent, while the lower branch displays an anomalous increase in strength. The frequencies and atomic characters of the lattice modes at the center of the Brillouin zone have been calculated for the high-temperature phase for each of these materials. The high-frequency E_u mode does not change in position or character across this series of compounds. Below T_N , the E_u modes are predicted to split into features of roughly equal strength. We discuss the possibility that the anomalous increase in the strength of the lower branch of the high-frequency mode below T_N in the Sr and Ba compounds, and the weak (silent) upper branch, may be related to the orbital ordering and a change in the bonding between the Fe and As atoms in the magnetically-ordered state.

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I. INTRODUCTION

The discovery of superconductivity in the iron-based materials¹ with superconducting critical temperatures (T_c 's) in excess of 50 K^{2,3} has prompted an intensive investigation of the physical properties of these multi-band materials in an effort to understand the pairing mechanism of the superconductivity⁴⁻⁸. The parent compounds are generally paramagnetic metals at room temperature. As the temperature is reduced they typically undergo a structural and magnetic transition into anti-ferromagnetic (AFM) state, but remain metallic. The $A\text{Fe}_2\text{As}_2$ ($A = \text{Ca}, \text{Sr}, \text{ or Ba}$) materials are particularly interesting; not only do they undergo structural and magnetic transitions, but superconductivity may also be induced through a variety of chemical substitutions, as well as through the application of pressure. The compound CaFe_2As_2 is tetragonal at high temperature; depending on growth conditions, it either undergoes a magnetic and structural transition to an orthorhombic phase with spin-density-wave-like magnetic order at $T_N \simeq 172$ K⁹⁻¹³, or it undergoes a dramatic decrease of the c -axis lattice parameter and enters into a non-magnetic, collapsed-tetragonal (cT) phase below 100 K^{14,15}; the cT phase, which is unique to this material, may also be stabilized by the application of pressure^{16,17} or through chemical substitution on various sites¹⁸⁻²¹. Superconductivity may be induced through either the application of pressure^{14,16,22-24}, or through chemical substitution, resulting in electron²⁵⁻²⁸, hole²⁹, or isovalent¹⁹ doping; co-

doping with La and P has been reported to yield a critical temperature as high as $T_c \simeq 45$ K³⁰. In SrFe_2As_2 , the structural and magnetic transition is observed at a somewhat higher temperature, $T_N \simeq 195$ K³¹⁻³³; superconductivity may be induced through a variety of chemical substitutions^{26,34-37}, as well as pressure^{38,39}, with T_c 's in the hole-doped materials as high as $\simeq 37$ K. The structural and magnetic transition in BaFe_2As_2 is lower than what is observed in the other two materials, $T_N \simeq 138$ K⁴⁰; superconductivity may be induced through the application of pressure^{38,41-43}, or by chemical substitution^{23,44-55}, with T_c 's as high as $\simeq 40$ K in the hole-doped materials.

As with the cuprates, the proximity of superconductivity to an AFM region suggests that the superconductivity may be mediated by spin fluctuations⁵⁶⁻⁵⁹, a notion that is supported by the argument that electron-phonon coupling in this class of materials is too small to give rise to the high transition temperatures⁶⁰. However, the behavior of the infrared-active lattice modes can, nonetheless, be quite striking; an example of this is the infrared phonon anomaly in BaFe_2As_2 observed below the structural and magnetic transition⁶¹⁻⁶⁵. In addition, the observation of a large iron isotope effect in several iron-based superconductors suggests an unconventional role for electron-phonon coupling may be possible⁶⁶.

In this work we extend our recent investigation of the electronic properties of the $A\text{Fe}_2\text{As}_2$ ($A = \text{Ca}, \text{Sr}, \text{ or Ba}$) parent compounds⁶⁷, to include the detailed behavior of the in-plane infrared-active vibrational modes above and

below T_N . In each of the materials, two infrared-active E_u modes are observed above T_N . Below the structural and magnetic transition, the low-frequency E_u mode splits into an upper and a lower branch of somewhat different strengths. In the Ca and Sr materials, the oscillator strength is conserved across the transition; however, in the Ba material the strength of this mode appears to weaken slightly below T_N . In the Ca and Sr materials, the high-frequency E_u mode splits into an upper and lower branch below T_N ; the two branches have dramatically different intensities. The oscillator strength is conserved through the transition in the Ca material, but displays an anomalous increase in strength below T_N in the Sr material. In Ba material, the high-frequency E_u mode no longer appears to split below T_N ; instead, it appears to undergo an abrupt decrease in frequency to become the lower branch, with the upper branch now being either very weak or completely absent. Furthermore, the oscillator strength of this mode increases anomalously below T_N ⁶¹. Both the high and low-frequency modes in this material display an asymmetric line shape below the structural and magnetic transition, indicating that the lattice modes may be coupling to spin or charge excitations. The vibrational frequencies and atomic intensities have been calculated at the center of the Brillouin zone for the high-temperature tetragonal phase using an *ab initio* method for the three different compounds. The high-frequency mode involves only in-plane Fe and As displacements that shows little change in frequency or vibrational character across the Ca \rightarrow Sr \rightarrow Ba series. However, the position of the low-frequency mode decreases significantly, with the character of the low-frequency mode shifting from an almost pure alkali-earth mode in the Ca material, to a more mixed character in the Sr and Ba compounds, that includes a significant component from the FeAs planes. Surprisingly, simple empirical force-constant models predict that both infrared-active E_u modes should split into two new vibrations of roughly equal strength, contrary to what is observed for the high-frequency E_u mode. We consider the possibility that the lack of splitting and the anomalous increase in strength observed in the high-frequency E_u mode below T_N may be related to the orbital ordering and the change in the nature of the bonding between the As and Fe atoms in the magnetically-ordered state.

II. EXPERIMENT

Single crystals of AFe_2As_2 ($A = \text{Ca, Sr, or Ba}$) were grown using conventional high-temperature solution growth techniques either out of self flux ($A = \text{Ba}$)⁴⁵, or out of Sn flux ($A = \text{Ca, Sr}$)^{9,15,68}, and characterized by x-ray scattering, electrical resistivity and magnetic susceptibility measurements. The reflectance of mm-sized, as-grown crystal faces has been measured at a near-normal angle of incidence for light polarized in the a - b planes over a wide frequency range from the far

infrared ($\simeq 3$ meV) to the ultraviolet ($\simeq 5$ eV) for a wide variety of temperatures above and below T_N using an *in situ* evaporation technique⁶⁹. Only naturally-occurring crystal faces have been used; the samples have not been cleaved or polished. The complex conductivity is determined from a Kramers-Kronig analysis of the reflectance⁷⁰, the details of which have been discussed in a previous publication⁶⁷.

III. RESULTS AND DISCUSSION

A. Fano profile

The vibrational properties of these materials are determined from the symmetry properties of the space group. Above T_N , the three materials studied all crystallize in the tetragonal $I4/mmm$ space group. The irreducible vibrational representation is

$$\Gamma_{\text{HT}} = A_{1g} + B_{1g} + 2E_g + 2A_{2u} + 2E_u,$$

where the E_u and A_{2u} vibrations are infrared active in the a - b planes and along the c axis, respectively. Accordingly, the two infrared active modes observed in these materials at room temperature are assigned as E_u modes. Below T_N , there is a weak structural transition to an orthorhombic $Fmmm$ space group, with the irreducible vibrational representation,

$$\Gamma_{\text{LT}} = A_g + B_{1g} + 2B_{2g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u},$$

where the B_{1u} modes are active along the c axis, and the orthorhombic distortion lifts the degeneracy of the E_u mode and splits it into $B_{2u} + B_{3u}$ (active along the b and a axes, respectively) for a total of four infrared-active modes at low temperature. However, *ab initio* studies indicate that the splitting of the E_u mode in the related LaFeAsO compound should be relatively small⁷¹, of the order of 1.5 cm^{-1} (0.2 meV).

In the absence of coupling to a continuum of excitations, infrared-active modes usually display a symmetric Lorentzian profile. However, it is possible that coupling to either a spin or charge background may be present, so the infrared-active vibrations have been fit using a phenomenological complex dielectric function, $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$, for a Fano-shaped Lorentz oscillator^{73,74},

$$\tilde{\epsilon}(\omega) = \frac{\Omega_0^2}{\omega_0^2 - \omega^2 - i\gamma_0\omega} \left(1 + i\frac{\omega_q}{\omega} \right)^2 + \left(\frac{\Omega_0\omega_q}{\omega_0\omega} \right)^2, \quad (1)$$

where ω_0 , γ_0 and Ω_0 are the position, width, and strength of the vibration, respectively, and the asymmetry is described by the dimensionless parameter $1/q = \omega_q/\omega_0$. The complex conductivity is $\tilde{\sigma}(\omega) = \sigma_1 + i\sigma_2 = -2\pi i\omega[\tilde{\epsilon}(\omega) - \epsilon_\infty]/Z_0$ (in units of $\Omega^{-1}\text{cm}^{-1}$); $Z_0 \simeq 377 \Omega$ is the impedance of free space. The complex conductivity satisfies $\tilde{\sigma}^*(\omega) = \tilde{\sigma}(-\omega)$. The real and imaginary parts of the optical conductivity are then:

Table I. The experimental and calculated (relaxed) lattice constants and atomic fractional coordinates of $A\text{Fe}_2\text{As}_2$ ($A = \text{Ca}$, Sr , and Ba) for the non-magnetic high-temperature tetragonal ($I4/mmm$) phase. The fractional coordinates for the A and Fe atoms are (000) and $(0 \frac{1}{2} \frac{1}{4})$, respectively.

Cell parameters	CaFe_2As_2		SrFe_2As_2		BaFe_2As_2	
	Experiment ^a	DFT	Experiment ^b	DFT	Experiment ^c	DFT
a (Å)	3.872	3.880	3.927	3.897	3.964	3.964
c (Å)	11.73	11.49	12.37	12.27	13.02	12.64
c/a	3.029	2.962	3.150	3.057	3.285	3.187
As $(00z)$	0.3612	0.3587	0.361	0.3528	0.361	0.3463
Fe-As (Å)	2.369	2.308	2.396	2.321	2.452	2.326
As-Fe-As ($^\circ$)	109.6	114.5	110.1	115.7	107.8	116.9

^a Ref 72.

^b Ref 31.

^c Ref 40.

$$\sigma_1(\omega) = \frac{2\pi}{Z_0} \frac{\Omega_0^2 [\gamma_0 \omega^2 - 2(\omega^2 \omega_0 - \omega_0^3)/q - \gamma_0 \omega_0^2/q^2]}{(\omega^2 - \omega_0^2)^2 + \gamma_0^2 \omega^2}, \quad (2)$$

and

$$\sigma_2(\omega) = \frac{2\pi}{Z_0} \frac{\omega \Omega_0^2 [(\omega^2 - \omega_0^2) - 2\gamma_0 \omega_0/q + (\omega^2 - \omega_0^2 + \gamma_0^2)/q^2]}{(\omega^2 - \omega_0^2)^2 + \gamma_0^2 \omega^2}. \quad (3)$$

Note that for finite ω_0 , in the $\omega_q \rightarrow 0$ (or $1/q^2 \rightarrow 0$) limit, the dielectric function for a simple Lorentz oscillator is recovered; however, as $1/q^2$ increases the line shape becomes increasingly asymmetric.

The infrared-active modes are superimposed on an electronic background, which in our previous study of these materials⁶⁷ was modeled using the two-Drude model⁷⁵,

$$\tilde{\epsilon}(\omega) = \epsilon_\infty - \sum_{j=1}^2 \frac{\omega_{p,D;j}^2}{\omega^2 + i\omega/\tau_{D,j}} + \sum_k \frac{\Omega_k^2}{\omega_k^2 - \omega^2 - i\omega\gamma_k}, \quad (4)$$

where ϵ_∞ is the contribution to the real part of the dielectric function from high-frequency excitations. In the first sum, $\omega_{p,D;j}^2 = 4\pi n_j e^2/m_j^*$ and $1/\tau_{D,j}$ are the square of the plasma frequency and scattering rate for the delocalized (Drude) carriers in the j th band, respectively, and n_j and m_j^* are the carrier concentration and effective mass. In the second summation, ω_k , γ_k and Ω_k are the position, width, and strength of the k th vibration or bound excitation.

B. Lattice dynamics

The electronic properties of $A\text{Fe}_2\text{As}_2$ ($A = \text{Ca}$, Sr , and Ba) for the non-magnetic high-temperature tetragonal ($I4/mmm$) phase have been calculated using density functional theory (DFT) with the generalized gradient approximation (GGA) using the full-potential linearized augmented plane-wave (FP-LAPW) method⁷⁶ with local-orbital extensions⁷⁷ in the

WIEN2k implementation⁷⁸. An examination of different Monkhorst-Pack k -point meshes indicated that a $5 \times 5 \times 5$ k -point mesh with $R_{mt}k_{max} = 8$ was sufficient for good energy convergence. Beginning with the experimental unit cell, the lattice parameters are adjusted and the total energy calculated for each structure; the lowest total energy in this phase space corresponds to the most stable geometry. The atomic fractional coordinates were then relaxed with respect to the total force, typically resulting in residual forces of less than 0.1 mRy/a.u. per atom. This procedure was repeated until no further improvement was obtained. A comparison of the experimental and calculated (relaxed) unit cell parameters are shown in Table I. While the calculated results for the a axis are in excellent agreement with the experimentally-determined values, the c axis is systematically smaller, a result that has been noted in other works^{79,80}.

The phonons have been determined using the direct method, also known as the frozen-phonon technique. To determine the phonons at the zone center, a $1 \times 1 \times 1$ supercell is sufficient. To obtain a complete set of Hellmann-Feynman forces, a total of 6 independent displacements are required; because there are always some residual forces at the atomic sites we have considered symmetric displacements, which doubles this number, resulting in a total of 12 atomic displacements. In this case, displacement amplitudes of 0.02 Å were used. Typical values for the displacements range from 0.02 to 0.06 Å; however, because of the highly-distorted nature of the Fe-As planes, a smaller displacement was chosen to ensure that the response was still linear. Due to the lower symmetry in these calculations an $8 \times 8 \times 2$ k -point mesh

Table II. Calculated frequencies and atomic intensities of $A\text{Fe}_2\text{As}_2$ ($A = \text{Ca}, \text{Sr}, \text{and Ba}$) for the zone-center modes in the non-magnetic high-temperature tetragonal ($I4/mmm$) phase compared with experimentally-observed values.

Mode	CaFe ₂ As ₂					SrFe ₂ As ₂					BaFe ₂ As ₂				
	ω_{exp} (cm ⁻¹)	ω_{calc} (cm ⁻¹)	Atomic intensity			ω_{exp} (cm ⁻¹)	ω_{calc} (cm ⁻¹)	Atomic intensity			ω_{exp} (cm ⁻¹)	ω_{calc} (cm ⁻¹)	Atomic intensity		
			Ca	Fe	As			Sr	Fe	As			Ba	Fe	As
E_g	—	323	0.00	0.73	0.27	264 ^c	316	0.00	0.72	0.28	264 ^a	313	0.00	0.70	0.30
E_u	264 ^a	300	0.00	0.56	0.44	257 ^a	296	0.00	0.56	0.44	258 ^a	296	0.00	0.55	0.45
A_{2u}	—	279	0.00	0.58	0.42	—	277	0.00	0.59	0.41	—	280	0.00	0.59	0.41
B_{1g}	211 ^b	211	0.00	1.00	0.00	204 ^c	229	0.00	1.00	0.00	217 ^d	232	0.00	1.00	0.00
A_{1g}	189 ^b	207	0.00	0.00	1.00	182 ^c	212	0.00	0.00	1.00	183 ^d	210	0.00	0.00	1.00
E_g	—	142	0.00	0.27	0.73	114 ^c	142	0.00	0.28	0.72	131 ^d	140	0.00	0.30	0.70
E_u	143 ^a	131	0.87	0.07	0.06	109 ^a	102	0.75	0.12	0.13	94 ^a	89	0.66	0.17	0.17
A_{2u}	—	126	0.87	0.05	0.08	—	104	0.75	0.09	0.16	—	95	0.66	0.13	0.21

^a This work; positions determined just above T_N .

^b Ref. 11; the A_{1g} (A_g) and B_{1g} modes are only observed below T_N .

^c Ref. 81.

^d Refs. 82 and 83; the A_{1g} (A_g) mode is only observed below T_N .

was used. The calculations have converged when the successive changes for the forces on each atom are less than 0.02 mRy/a.u. The residual forces are collected for each set of symmetric displacements and a list of the Hellmann-Feynman forces are generated. Using the program PHONON⁸⁴ the cumulative force constants deconvoluted from the Hellmann-Feynman forces are introduced into the dynamical matrix, which is then diagonalized in order to obtain the phonon frequencies. The atomic intensities are further calculated to describe the character of the vibration; in this case the intensity refers to the square of the vibrational amplitude of each atom for a given mode. The results are shown in Table II. A general result in these materials is that calculations based on relaxed unit cells tend to return frequencies that are, for the most part, larger than the experimentally-observed energies^{85,86}. While better agreement with experiment may be achieved if the experimental values for the unit cell parameters are used^{80,86,87}, this approach is not recommended because of the large residual forces that may be present in an unrelaxed unit cell.

C. CaFe₂As₂

The real part of the optical conductivity of CaFe₂As₂ is shown in Fig. 1(a) for light polarized in the a - b planes, with the electronic background removed, in the region of the low-frequency E_u mode at $\simeq 142$ cm⁻¹ (the curves have been offset for clarity). At room temperature, only one mode may be observed; below T_N , this mode clearly splits into two features at $\simeq 138$ and 146 cm⁻¹ in response to the orthorhombic distortion, in agreement with a previous study⁶⁵. The fit to the real and imaginary parts of the optical conductivity at 5 K is shown in Figs. 1(b) and 1(c), respectively, using the Fano line shapes in Eqs. (2) and (3) with an electronic background described by the two-Drude model; the line shapes are reproduced quite well. The position of the low-frequency

E_u mode is gradually increasing with decreasing temperature until it splits below T_N ; the upper branch increases slightly in frequency (hardens), while the lower branch decreases (softens) as the temperature is lowered, shown in Fig. 1(d). We adopt the scheme of applying the color of the fundamental to track the strongest feature below T_N . The line width shown in Fig. 1(e) is decreasing with temperature; below T_N there is no discontinuity as the widths of the new modes are roughly equal and continue to decrease with temperature. Below T_N the oscillator strength of the lower branch is less than that of the upper branch [reflected in the color scheme of Fig. 1(d)]. Individually, the strengths of these modes are less than that of the high-temperature mode, but if the strengths are added in quadrature, that is $\Omega_1^2 + \Omega_2^2$, then they reproduce the strength of the original E_u mode, as shown in Fig. 1(f). The small value of the asymmetry parameter in Fig. 1(g) indicates that the modes are all symmetric, both above and below T_N .

The optical conductivity is shown with the electronic background removed in Fig. 1(h) in the region of the high-frequency E_u mode at $\simeq 258$ cm⁻¹ (the curves have been offset for clarity). At room temperature a single mode is observed; below T_N two new modes appear at $\simeq 261$ and 267 cm⁻¹; the fit to the real and imaginary parts of the optical conductivity at 5 K using two oscillators reproduces the data quite well, as shown in Figs. 1(i) and 1(j), respectively. In general, while there are a number of other weak features in Figs. 1(a) and 1(h) that might be argued to be due to vibrational structure, we limit our attention to only those features that show a systematic temperature dependence. Above T_N the frequency of the E_u mode increases relatively quickly with decreasing temperature; below T_N this mode appears to continue as a very weak upper branch that continues to harden, while the fundamental undergoes an abrupt decrease in frequency to form a strong lower branch that hardens slightly with decreasing temperature, shown in Fig. 1(k). Interestingly, the dotted line connecting the

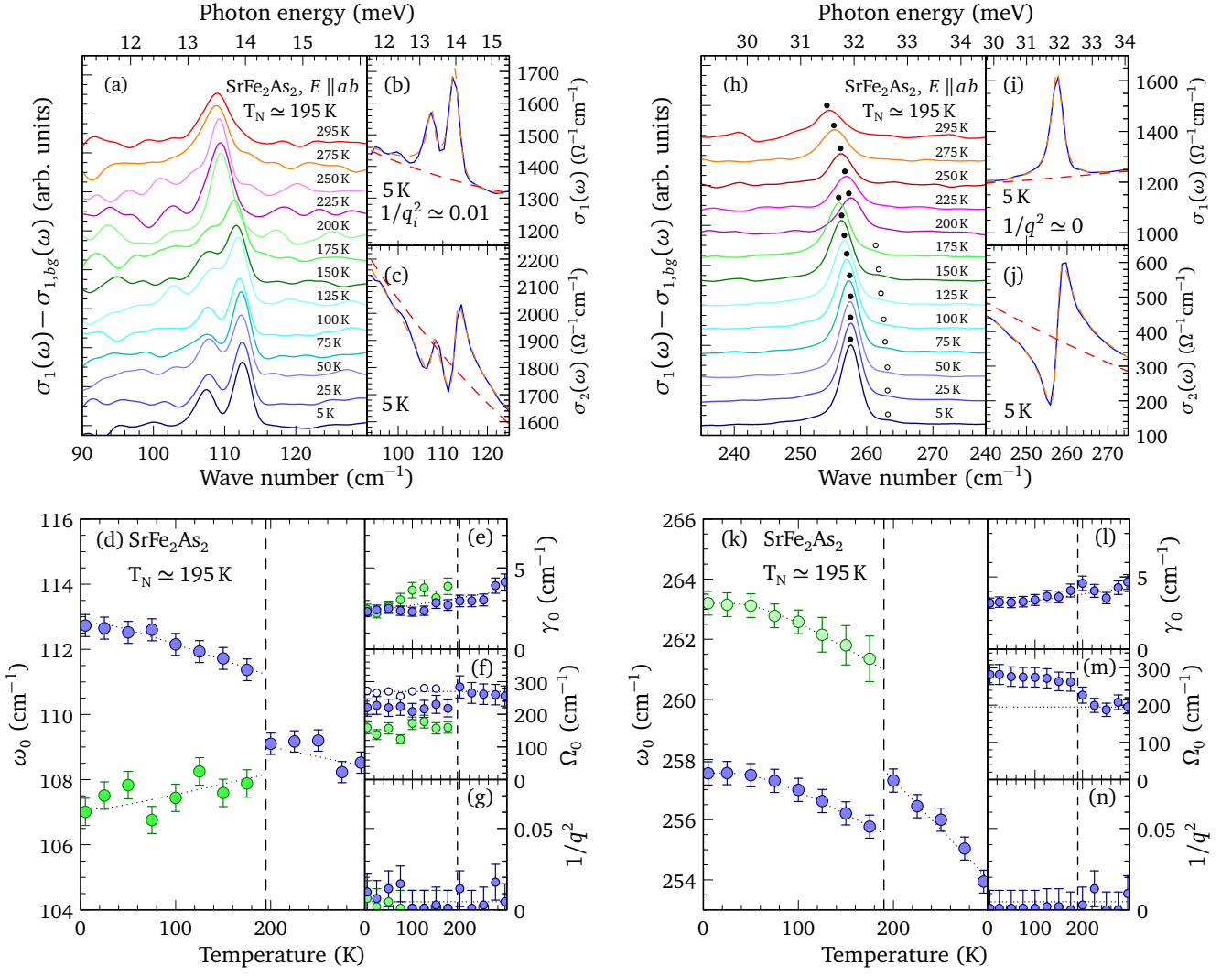


Figure 2. (a) The temperature dependence of the low-frequency E_u mode in the optical conductivity for SrFe_2As_2 ($T_N \simeq 195$ K) with the electronic background removed. (b) The results of the fit at 5 K to the real part of the optical conductivity, and (c) the imaginary part. The temperature dependence of the (d) positions; (e) line widths; (f) strength of the modes (for $T < T_N$, the open circles are the strengths of the two modes added in quadrature); (g) asymmetry parameters. (h) The temperature dependence of the high-frequency E_u mode in the optical conductivity with the electronic background removed; the position of the fundamental is indicated by solid circles, below T_N the position of the upper band is denoted by the open circles. (i) The results of the fit at 5 K to the real part of the optical conductivity, and (j) the imaginary part. The temperature dependence of the (k) position; (l) line width; (m) oscillator strength; (n) asymmetry parameter. Unless otherwise indicated in the text, the dotted lines are drawn as a guide to the eye.

calculated position of the high-frequency E_u mode is larger the experimentally-observed value of 264 cm^{-1} ; the atomic intensities indicate that this in-plane mode involves roughly equal contributions from the Fe and As atoms, with no contribution from the Ca atom (Table II).

D. SrFe_2As_2

The real part of the optical conductivity of SrFe_2As_2 is shown in Fig. 2(a) for light polarized in the a - b planes, with the electronic background removed, in the region of

the low-frequency E_u mode at $\simeq 109 \text{ cm}^{-1}$ (the curves have been offset for clarity). At room temperature, only a single mode is observed; this crystal is somewhat smaller than the other two, consequently the data is slightly noisier in the long-wavelength region. Below $T_N \simeq 195$ K this mode clearly splits into two features at $\simeq 107$ and 112 cm^{-1} . Using the previously described approach, the Fano line shape is fit to the real and imaginary parts of the optical conductivity at 5 K as shown in Figs. 2(b) and 2(c), respectively; the line shapes are reproduced quite well. As a result of the rather large value for T_N in this material, the position of the low-frequency E_u

mode shows relatively little temperature dependence before splitting abruptly below the structural and magnetic transition; the upper branch continues to harden with decreasing temperature, while the lower branch softens, shown in Fig. 2(d). The line width shown in Fig. 2(e) is decreasing with temperature; below T_N there is no discontinuity as the widths of the new modes are roughly equal and continue to decrease with temperature. Below T_N the oscillator strength of the lower branch is less than that of the upper branch, but if the strengths of these two modes are added in quadrature, they reproduce the strength of the fundamental mode, as shown in Fig. 2(f). The asymmetry parameter in Fig. 2(g) indicates that the modes are all symmetric, both above and below T_N .

The optical conductivity is shown with the electronic background removed in Fig. 2(h) in the region of the high-frequency E_u mode at $\simeq 254 \text{ cm}^{-1}$ (the curves have been offset for clarity). For $T \ll T_N$, there is some evidence that this mode splits, but the shoulder just above the main peak is extremely weak and difficult to refine. As a consequence, we have used only a single oscillator to fit the data, while estimating the position of the shoulder from the peak in the conductivity (the width and oscillator strength of this feature are not reported). The fit to the real and imaginary parts of the optical conductivity at 5 K using the Fano line shape reproduces the data quite well, as shown in Figs. 2(i) and 2(j), respectively. Above T_N the position of this mode hardens with decreasing temperature before splitting below T_N into a strong lower branch and a weak upper branch, both of which continue to harden with decreasing temperature, shown in Fig. 2(k). The width the mode shown in Fig. 2(l) is decreasing continuously with temperature and shows no anomalous behavior at T_N . The temperature dependence of the frequency and position is consistent with the anharmonic decay scheme (dotted lines). Above T_N , the strength of this mode is identical to that observed in CaFe_2As_2 ; however, below T_N this mode displays an unusual increase in strength. The asymmetry parameter in Fig. 2(n) indicates that the mode is symmetric, both above and below T_N .

The calculated position of the high-frequency E_u mode for SrFe_2As_2 in the tetragonal phase of 296 cm^{-1} is once again larger the experimentally-observed position at 257 cm^{-1} (taken just above T_N); however, the nature of this mode is unchanged from CaFe_2As_2 with nearly identical atomic intensities (Table II). The calculated position of the low-frequency E_u mode of 102 cm^{-1} is in reasonable agreement with the experimentally-observed value of 109 cm^{-1} ; however, this value is significantly lower than it is in CaFe_2As_2 (102 compared to 131 cm^{-1}), and the character of this mode is altered with the Sr atom now playing a decreased role, with larger contributions from the Fe and As atoms.

E. BaFe_2As_2

The real part of the optical conductivity of BaFe_2As_2 is shown in Fig. 3(a), with the electronic background removed, in the region of the low-frequency E_u mode at $\simeq 94 \text{ cm}^{-1}$ (the curves have been offset for clarity). As in the other two cases, at room temperature a single mode is observed; below T_N it splits into two modes at $\simeq 93$ and 97 cm^{-1} . Using the previously described approach, the Fano line shape is fit to the real and imaginary parts of the optical conductivity at 5 K and is shown in Figs. 3(b) and 3(c), respectively, reproducing the data quite well. The position of the low-frequency E_u mode above and below T_N is shown in Fig. 3(d); overall, this mode shows little frequency dependence, in agreement with a previous study⁶⁴. The line width shown in Fig. 3(e) is decreasing with temperature; below T_N there is no discontinuity as the widths of the new modes are roughly equal and continue to decrease with temperature. Below T_N the oscillator strength of the lower branch is less than that of the upper branch. Unlike the other two materials, when the strengths of the two modes are added in quadrature, they fail to reproduce the strength of the fundamental mode, as shown in Fig. 3(f). The asymmetry parameter in Fig. 3(g) indicates this mode is symmetric at high temperature; however, below T_N both modes display a pronounced asymmetry.

The optical conductivity is shown with the electronic background removed in Fig. 3(h) in the region of the high-frequency E_u mode at $\simeq 254 \text{ cm}^{-1}$ (the curves have been offset for clarity). At high temperature a single mode is observed; below T_N , unlike the previous two materials, we fail to observe an unambiguous splitting. Other workers have observed a weak shoulder in optical conductivity at $\simeq 262 \text{ cm}^{-1}$ which they attribute to the splitting of this mode⁶⁴; however, we consider only a single oscillator. The fit to the real and imaginary parts of the optical conductivity at 5 K using the Fano line shape reproduces the data quite well, as shown in Figs. 3(i) and 3(j), respectively. The position of this mode hardens with decreasing temperature until it softens anomalously at T_N before continuing to harden slightly at low temperature. The softening is understood as a splitting in response to the orthorhombic distortion in which the upper branch is curiously silent. The width of the mode, shown in Fig. 3(l), decreases with temperature, showing no discontinuity at T_N . The temperature dependence of the frequency and position are both consistent with the anharmonic decay scheme (dotted lines). Above T_N , the strength of this mode is identical to that observed in the other two materials; however, below T_N this mode increases dramatically in strength, shown in Fig. 3(m). The asymmetry parameter in Fig. 3(n) indicates that the mode is symmetric above T_N , but develops a slight asymmetry at low temperature.

The calculated position of the low-frequency E_u mode at 89 cm^{-1} is in good agreement with the experimentally observed position at $\simeq 94 \text{ cm}^{-1}$; however, in a continu-

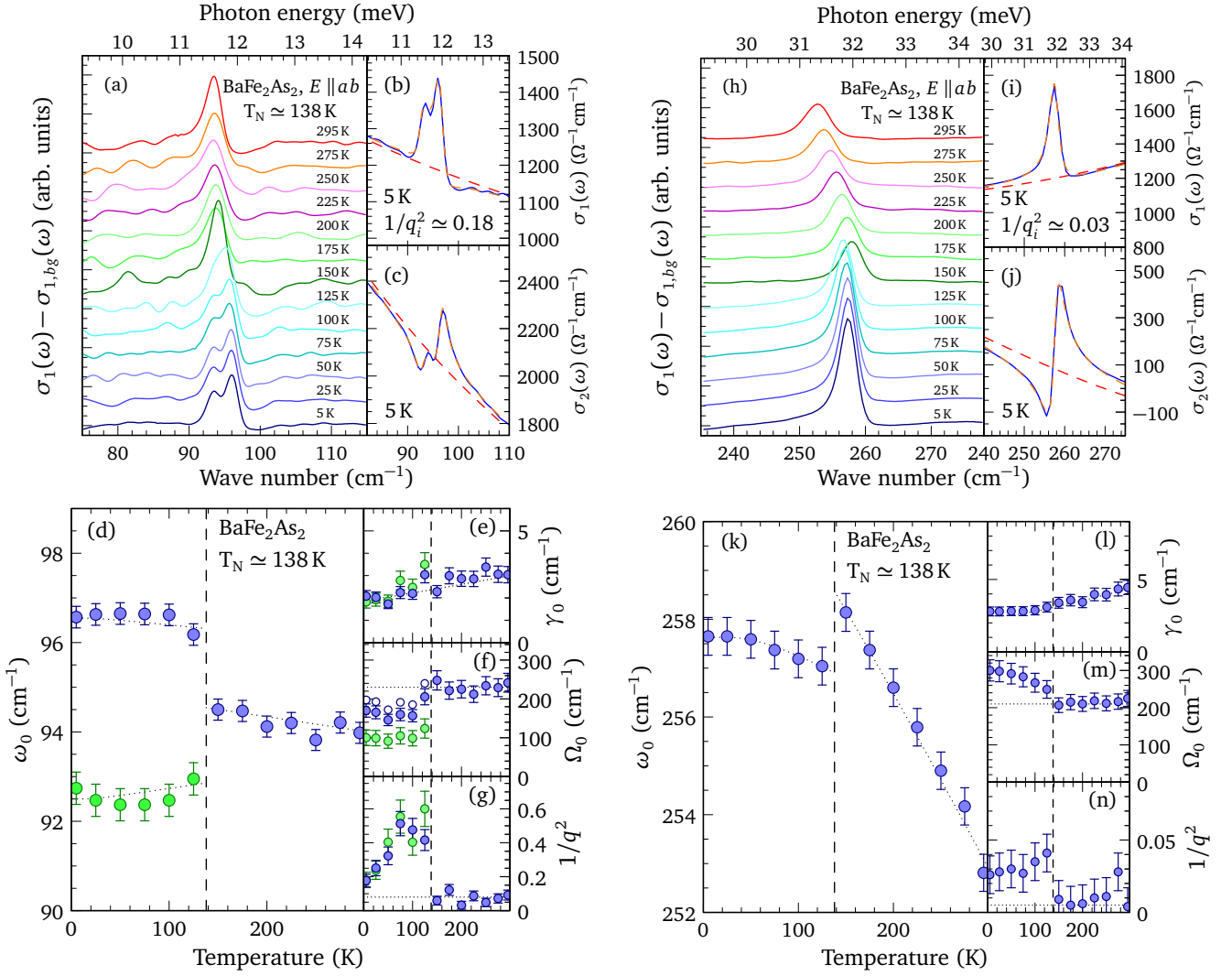


Figure 3. (a) The temperature dependence of the low-frequency E_u mode in the optical conductivity for BaFe₂As₂ ($T_N \approx 138$ K) with the electronic background removed. (b) The results of the fit at 5 K to the real part of the optical conductivity, and (c) the imaginary part. The temperature dependence of the (d) positions; (e) line widths; (f) strength of the modes (for $T < T_N$, the open circles are the strengths of the two modes added in quadrature); (g) asymmetry parameters. (h) The temperature dependence of the high-frequency E_u mode in the optical conductivity with the electronic background removed. (i) The results of the fit at 5 K to the real part of the optical conductivity, and (j) the imaginary part. The temperature dependence of the (k) position; (l) line width; (m) oscillator strength; (n) asymmetry parameter. Unless otherwise indicated in the text, the dotted lines are drawn as a guide to the eye.

ation of the trend observed in SrFe₂As₂, the character of this mode has changed significantly with the Ba atom now playing a reduced role with increased contributions from the Fe and As atoms (Table II). The calculated position of the high-frequency mode of 298 cm⁻¹ is larger than the experimentally observed value at 258 cm⁻¹; interestingly, the vibrational character for this mode remains unchanged across all three materials.

F. Phonon anomalies

In AFe₂As₂, the series of $A = \text{Ca, Sr and Ba}$ represents the steadily increasing size of the alkali earth atom, which is reflected by the increase in the c -axis lattice parameter (Table I). The vibrational properties of CaFe₂As₂ are an interesting point of departure in that they may be described as more or less conventional; both E_u modes harden with decreasing temperature as expected^{86,88,89} and the $E_u \rightarrow B_{2u} + B_{3u}$ splitting is observed below T_N for both modes. While one mode is typically stronger than the other, when the strengths of the modes are added in quadrature, the strength of the original E_u

mode is recovered. It is not unusual for the strengths of the B_{2u} and B_{3u} modes to be different; however, in the case of the high-frequency E_u mode they are significantly different, $\Omega_2^2/\Omega_1^2 \simeq 0.05$ [Fig. 1(m)]. This is rather surprising as a simple empirical force-constant model⁹⁰ that reproduces the positions of the vibrations below T_N indicates that while there is some difference in the strengths of the low-frequency modes, the strengths of the high-frequency B_{2u} and B_{3u} modes should be nearly identical. In SrFe_2As_2 , the low-frequency E_u mode hardens with decreasing temperature and underdoes a $B_{2u} + B_{3u}$ splitting below T_N ; the oscillator strength is conserved. Beyond this point, any similarity with the Ca compound vanishes; while the high-frequency E_u mode appears to split below T_N , the response is dominated by the lower branch, while the shoulder that comprises the upper branch is extremely weak. In addition, the strength of the lower branch is observed to increase anomalously below T_N [Fig. 2(m)] by nearly a factor of two.

The most striking phonon anomalies occur in BaFe_2As_2 . While the splitting of the low-frequency E_u mode is observed below T_N ⁶⁴, the strengths of the new modes now sum to less than the original E_u mode [Fig. 3(f)]. Additionally, both modes appear to have asymmetric line shapes; considering that these modes have an increased Fe and As atomic character, the possibility of lattice mode coupling to spin or charge excitations within the conducting FeAs planes can not be discounted. Furthermore, the high-frequency E_u mode fails to demonstrate any splitting below T_N and undergoes a dramatic increase in oscillator strength of $\simeq 2.3$ ^{61,64}. Below T_N the spins order antiferromagnetically along the a axis and ferromagnetically along the b axis^{10,91}. Optical studies of mechanically-detwinned single crystals of this compound indicate that there is a significant optical anisotropy with the optical conductivity along the a axis being roughly twice that along the b axis over much of the infrared region^{63,92,93}. The high-frequency mode is only observed along the b axis below T_N , and is thus a B_{2u} mode⁶³. The absence of the B_{3u} mode has been attributed to screening effects⁶⁴; however, given that the conductivity anisotropy in the region of the mode is only about a factor of two, screening seems unlikely⁹⁴.

The bonding in the highly-distorted FeAs planes occurs from the hybridization of the Fe d_{xz} and d_{yz} and As $4p$ orbitals^{95,96}; below T_N there is a strongly orbital-dependent reconstruction of the electronic structure^{97–99}, resulting in orbital ordering^{100–107}. In this scenario, degeneracy between the d_{xz} and d_{yz} orbitals is removed, resulting in unequal occupations. The strength of an infrared-active mode is calculated from the Born effective charge on the atoms, which when taken with the atomic displacements for a particular normal mode, is used to calculate the strength of the dipole moment. Changes in the strength of a mode require changes in either bonding or coordination; the weak nature of the structural phase transition rules out the latter, leaving only changes in bonding as a reasonable explanation. Because there is

a quasi-one-dimensional spin-density wave (SDW) along the a axis, it is possible that a weak spin-dimerization could result in a weak bond-centered charge-density wave (CDW) in this direction as well with twice the periodicity of the SDW. Furthermore, we speculate that the different charge densities associated with the bonds may result in dramatically different dipole moments along the a and b directions in the magnetically-ordered state, resulting in the increase in strength of the B_{2u} mode and the almost total extinction of the B_{3u} mode.

IV. CONCLUSIONS

The detailed temperature dependence of the in-plane infrared active modes has been studied in $A\text{Fe}_2\text{As}_2$ ($A = \text{Ca, Sr, and Ba}$) above and below the structural and magnetic transition at $T_N = 172, 195$ and 138 K, respectively. The phonon frequencies and atomic characters have also been determined from first principles for each compound in the high-temperature tetragonal phase. The CaFe_2As_2 material is the most conventional; the $E_u \rightarrow B_{2u} + B_{3u}$ splitting into upper and lower branches is observed below T_N for both of the infrared-active modes. For the low-frequency E_u mode, below T_N the lower branch continues to soften with decreasing temperature, while the upper branch hardens. The high-frequency E_u mode splits into upper and lower branches of very different strengths, both of which continue to harden with decreasing temperature in a fashion consistent with an anharmonic decay scheme. For both modes, the oscillator strengths are conserved across the transition, and none of the modes shows any obvious asymmetry. The behavior of the low-frequency E_u mode is similar in SrFe_2As_2 ; however, while the high-frequency E_u mode is still observed to split in this material, the upper branch is now extremely weak, and the oscillator strength of the lower branch increases anomalously below T_N . This behavior is repeated in BaFe_2As_2 , except that now the oscillator strengths of the low-frequency modes are no longer conserved; below T_N the high-frequency E_u mode softens anomalously into a lower branch (B_{2u})⁶³ that increases dramatically in strength with decreasing temperature, while the upper branch (B_{3u}) is now entirely absent. The presence of a SDW (and possibly a weak CDW) along the a axis below T_N suggests that the nature of the bonding along the a and b axis has been altered due to orbital ordering, which may be responsible for the increase in the strength of the B_{2u} mode and the almost total extinction of the B_{3u} mode.

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