



Infrared phonon anomaly in BaFe₂As₂

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The detailed optical properties of BaFe₂As₂ have been determined over a wide frequency range above and below the structural and magnetic transition at $T_N \approx 138$ K. A prominent in-plane infrared-active mode is observed at 253 cm^{-1} (31.4 meV) at 295 K. The frequency of this vibration shifts discontinuously at T_N ; for $T < T_N$ the frequency of this mode displays almost no temperature dependence, yet it nearly doubles in intensity. This anomalous behavior appears to be a consequence of orbital ordering in the Fe-As layers.

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The exciting discovery of superconductivity in the iron-arsenic (pnictide) compound LaFeAsO_{1-x}F_x with a high critical temperature¹ $T_c = 26$ K has generated a great deal of interest in this class of materials. Other rare-earth substitutions² quickly increased T_c above 50 K, and T_c s in excess of 50 K have been also achieved through the application of pressure.³ More recently, the oxygen free and structurally simpler BaFe₂As₂ material has been investigated. At room temperature, this material is tetragonal ($I4/mmm$), but undergoes a magnetic transition at $T_N \approx 138$ K that is accompanied at the same time by a weak structural distortion into an orthorhombic phase ($Fmmm$) with anomalies in the specific heat, resistivity, and susceptibility.^{4,5} While the magnetic transition in the pnictides was originally discussed as a spin-density-wave instability,^{4,6} there is currently some debate as to the microscopic nature of the magnetism.⁷ The magnetic and structural transitions are suppressed and superconductivity is recovered through the application of either pressure⁸ ($T_c \approx 29$ K) or chemical doping⁹⁻¹¹ ($T_c = 38$ K in the potassium-doped material), indicating that the superconductivity in this class of materials originates in the Fe-As layers. When the relatively high values for T_c are considered with the strong interplay between the lattice and magnetism, it is likely that the superconducting pairing interaction is not phonon mediated.¹² However, electron-phonon coupling may be present in the pnictides.^{13,14} Optical investigations of the nonsuperconducting BaFe₂As₂ compound^{15,16} and the doped superconducting materials¹⁷⁻¹⁹ have focused primarily on the large-scale features in the optical properties; the vibrational features in the undoped material have either not been observed¹⁶ or if they have been observed,¹⁵ they have not been discussed.

In this Rapid Communication we present the detailed in-plane optical properties of a single crystal of BaFe₂As₂. In addition to the large scale changes previously observed in the optical properties,¹⁵ we also observe both in-plane symmetry-allowed infrared-active modes at ≈ 94 and 253 cm^{-1} at 295 K. Anomalous behavior in both the position and strength of the 253 cm^{-1} mode is observed below T_N ; this mode involves displacements in the Fe-As layer. The possible origins of this behavior are discussed, with the most compelling being an orbital-ordering scenario resulting in a change in the nature of the bonding.²⁰⁻²³

Large single crystals of BaFe₂As₂ were grown by a self-flux method.¹¹ The reflectance has been measured above and below T_N over a wide frequency range (2 meV to over 3 eV) for light polarized in the a - b plane using an *in situ* evaporation technique.²⁴ The low-frequency results are shown in Fig. 1. At room temperature the low-frequency reflectance is metallic; however, there is a prominent shoulder at about 5000 cm^{-1} or 0.6 eV (not shown) that has been previously observed.^{15,16} As the temperature is reduced the low-frequency reflectance continues to increase, but for $T < T_N$ the reflectance between 200 – 800 cm^{-1} shows a remarkable suppression.¹⁵ We note that this type of behavior is also observed in chromium²⁵ below $T_N \approx 312$ K, and in the charge- and spin-stripe ordered state of La_{2-x}Ba_xCuO₄ for $x = 1/8$ (for which the superconductivity is dramatically suppressed) where the large changes in the reflectance were associated with the partial gapping of the Fermi surface.^{26,27} In addition

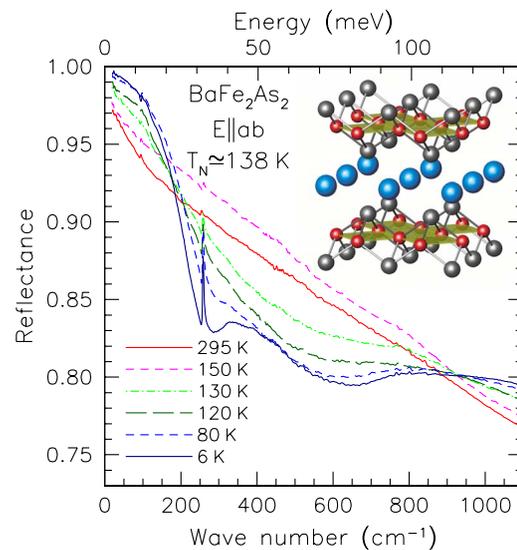


FIG. 1. (Color online) The reflectance in the low-frequency region for a single crystal of BaFe₂As₂ for light polarized in the a - b planes at several temperatures above and below the structural and magnetic transition at $T_N \approx 138$ K. The resolution at low frequency is typically better than 2 cm^{-1} . Inset: the arrangement of the Fe-As layers and the interstitial Ba atoms.

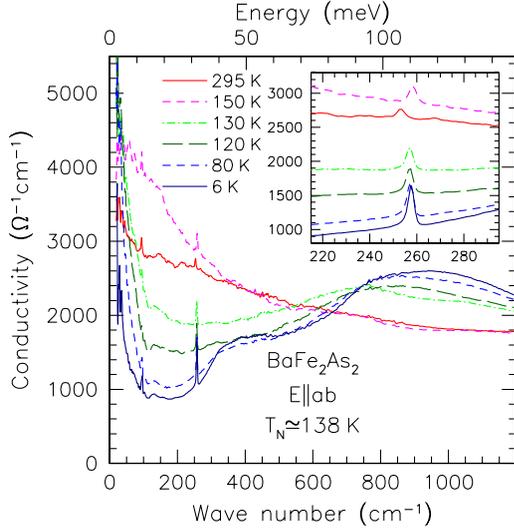


FIG. 2. (Color online) The real part of the optical conductivity in the low-frequency region for BaFe_2As_2 for light polarized in the a - b planes for several temperatures above and below the structural and magnetic transition at $T_N \approx 138$ K. Inset: the real part of the optical conductivity in the region of the infrared-active mode at ≈ 253 cm^{-1} .

to the gross features in the reflectance of BaFe_2As_2 , the two sharp features observed at ≈ 94 and 253 cm^{-1} (11.7 and 31.4 meV, respectively) are the in-plane infrared-active lattice vibrations.

The optical conductivity has been determined from a Kramers-Kronig analysis of the reflectance. The calculated conductivity is shown in the low-frequency region in Fig. 2. The optical conductivity can be modeled reasonably well by using a Drude-Lorentz model for the complex dielectric function

$$\tilde{\epsilon}(\omega) = \epsilon_\infty - \frac{\omega_{p,D}^2}{\omega^2 + i\omega/\tau_D} + \sum_j \frac{\Omega_j^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j}, \quad (1)$$

where ϵ_∞ is the real part of the dielectric function at high frequency, $\omega_{p,D}^2 = 4\pi n e^2 / m^*$ and $1/\tau_D$ are the plasma frequency and scattering rate for the delocalized (Drude) carriers, respectively; ω_j , γ_j , and Ω_j are the position, width, and oscillator strength of the j th vibration (the intensity is proportional to Ω_j^2). The complex conductivity is simply $\tilde{\sigma}(\omega) = \sigma_1 + i\sigma_2 = -i\omega[\tilde{\epsilon}(\omega) - \epsilon_\infty]/4\pi$.

Above T_N the conductivity may be reproduced below 1 eV by using a Drude term in combination with several bound excitations; a nonlinear least-squares fit yields $\omega_{p,D} = 8630$ cm^{-1} and $1/\tau_D = 398$ cm^{-1} at 295 K. The observed value of $\sigma_{dc} \equiv \sigma_1(\omega \rightarrow 0) \approx 3100$ $\Omega^{-1}\text{cm}^{-1}$ is in reasonable agreement with transport measurements.^{5,28} As the temperature is reduced $\omega_{p,D}$ remains relatively constant, but the scattering rate decreases to $1/\tau_D = 285$ cm^{-1} at 150 K. The character of the conductivity changes dramatically below T_N . The Drude component weakens and narrows, with $\omega_{p,D} = 3970$ cm^{-1} and $1/\tau_D = 39$ cm^{-1} at 80 K, resulting in a loss of spectral weight that appears to be transferred to mid-infrared band at ≈ 1000 cm^{-1} . [The spectral weight is de-

TABLE I. The vibrational parameters for oscillator fits to the symmetry-allowed infrared-active phonon modes observed in the a - b plane at 295 and 6 K, where ω_j , γ_j , and Ω_j are the frequency, width, and oscillator strength, respectively, of the j th mode. The estimated errors are indicated in parenthesis. All units are in cm^{-1} .

295 K (HTT)			6 K (LTO)		
ω_j	γ_j	Ω_j	ω_j	γ_j	Ω_j
94.0(0.1)	3.5(0.4)	222(8)	95.4(0.2)	3.9(0.9)	236(17)
253.2(0.1)	4.1(0.2)	226(7)	257.5(0.1)	2.7(0.2)	315(8)

finned simply as the weight under the optical conductivity curve over a given interval, $\int_0^{\omega_c} \sigma_1(\omega, T) d\omega$.] Despite the nearly 80% reduction in the number of free carriers, the resistivity continues to decrease due to the dramatic reduction in the scattering rate. These observations are consistent with those of a previous study;¹⁵ however, they are not the main focus of this work. Instead, we note in Fig. 2 that in addition to the broad features associated with the optical conductivity, there are two very sharp resonances observed at ≈ 94 and 253 cm^{-1} at 295 K. The vibrational features in the optical conductivity have been fit using Lorentz oscillators with a linear background and the results are shown in Table I at 295 and 6 K.

For $T > T_N$, BaFe_2As_2 is in the tetragonal $I4/mmm$ space group. The irreducible vibrational representation in the high-temperature tetragonal (HTT) phase is²⁹

$$\Gamma_{\text{vib}}^{\text{HTT}} = A_{1g} + B_{1g} + 2E_g + 2A_{2u} + 2E_u.$$

Of these, only the A_{2u} and E_u vibrations are infrared active (along the c axis and a - b planes, respectively), so the two modes we observe are the symmetry-allowed infrared-active E_u modes. For $T < T_N$ the material is in the orthorhombic $Fmmm$ space group, and the irreducible vibrational representation of the low-temperature orthorhombic (LTO) phase is

$$\Gamma_{\text{vib}}^{\text{LTO}} = A_g + B_{1g} + 2B_{2g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}.$$

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 quite small,³⁰ of the order of 1.5 cm^{-1} (0.2 meV), and indeed no new modes are observed in that material at low temperature.

Below T_N at 6 K, the low-frequency mode has hardened somewhat to 95.4 cm^{-1} and is now somewhat broader, suggesting that this mode may be showing signs of splitting; however, the oscillator strength has not changed appreciably. This mode involves displacements primarily of the Ba atoms.²⁹ The behavior of the 253 cm^{-1} mode is fundamentally different. Between 295 and 6 K this mode increases slightly in frequency and narrows slightly (as expected); however, the oscillator strength increases from $\Omega_j = 226 \rightarrow 315$ cm^{-1} , leading to a doubling in the intensity

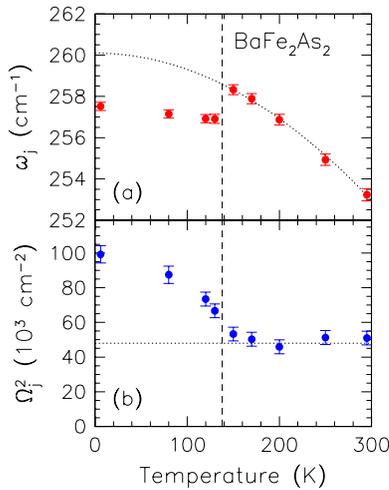


FIG. 3. (Color online) the temperature dependence of the (a) frequency (ω_j) and (b) intensity (Ω_j^2) of the infrared-active mode in BaFe₂As₂ observed at ≈ 253 cm⁻¹. In both cases the dashed line indicates $T_N \approx 138$ K, and the dotted line represents the temperature dependence expected in the absence of a structural or magnetic transition.

(inset of Fig. 2). The detailed temperature dependence of the frequency and the intensity of this mode is shown in Fig. 3. In Fig. 3(a), the mode increases in frequency with decreasing temperature, but at T_N there is an abrupt decrease in frequency; for $T < T_N$ the position of the mode displays little temperature dependence. In Fig. 3(b) the intensity remains constant from 295 to 150 K but increases in a mean-field way for $T < T_N$, nearly doubling in intensity at low temperature. The dotted lines in Fig. 3 represent the expected behavior; the frequency of a mode is generally expected to follow a quadratic temperature dependence (“hardening”). The intensity of an infrared-active mode is related to the net dipole moment $\mu_i = \sum_j Z_j^* u_{ij}$, where Z_j^* is the Born effective charge of the j th atom in the unit cell and u_{ij} is its displacement in the i th direction;³¹ the intensity of a mode is proportional to $\sum_i \mu_i^2$. From this expression, the intensity of a mode is expected to remain constant, unless there is a change in bonding or coordination. Alternatively, the intensity may also change if the electronic screening decreases, or if the lattice mode couples to either the spins or the electronic background. We will begin with the last point first. The interaction of a lattice mode with the electronic background often results in interference effects resulting in an asymmetric line shape;^{32,33} however, the observed phonon line shape in the optical conductivity is a symmetric Lorentzian (inset of Fig. 2), suggesting that any coupling between the lattice mode and the electronic background is small. Spin-phonon coupling has been observed in some quantum magnets to manifest itself primarily as a weak softening of a phonon mode;³⁴ however, there is virtually no effect on the intensity, suggesting this type of coupling is also rather weak.

A decrease in the electronic background may lead to a reduction in the screening and an increase in the oscillator strength. However, in many “bad metals” screening effects are quite small.³⁵ While there is a substantial decrease in the electronic background beneath both the 94 and 253 cm⁻¹

modes below T_N , the strength of the 253 cm⁻¹ mode increases dramatically while the strength of the 94 cm⁻¹ mode remains essentially unchanged. In addition, the electronic background beneath the 253 cm⁻¹ mode actually increases between 295 and 150 K, yet no change in intensity is observed. Finally, in the potassium-doped compound this mode may still be observed;¹⁷ however, in the cobalt-doped analog¹⁹ this mode is either not observed or extremely weak, despite the fact that the electronic backgrounds are similar. This evidence suggests that the 253 cm⁻¹ mode is probably unscreened but very sensitive to local disorder in the Fe-As layers, which is not surprising given that this vibration involves displacements of the Fe and As atoms.³⁶

This brings us to the possibility of changes to the bonding or coordination. The structural distortion in this material is rather weak and does not result in any significant changes in coordination for the atoms in the unit cell.⁴ It is possible that below T_N there might be a redistribution of charge.³⁷ Changes in Z_{Fe}^* , Z_{As}^* , or both would likely produce a change in Z_{Ba}^* ; however, the intensity of the Ba mode at 94 cm⁻¹ does not change appreciably below T_N , suggesting that Z_{Ba}^* is relatively constant. This makes it unlikely that the increase in intensity of the 253 cm⁻¹ mode results from a redistribution of charge. Recent experimental and theoretical studies on the electronic structure of BaFe₂As₂ and related systems^{20–23} conclude that the magnetism and the structural distortion is driven by hybridization and orbital ordering. In this treatment, the structural distortion and magnetic order result from a hybridization of the fourfold coordinated Fe 3*d* and the tetrahedrally positioned As 4*p* orbitals which strongly modifies the tails of the Wannier functions (local real-space orbitals) perpendicular to their original directions, resulting in a rare ferro-orbital ordering.²² The change in the nature of the bonding between the Fe and As atoms implies that the atomic displacements may be altered in a fashion that would lead to an increase in the intensity of the 253 cm⁻¹ mode; this mechanism may also explain the abrupt shift in the frequency at T_N . However, the full extent of the effects of the orbital ordering on the frequency and strength of this infrared-active mode will have to wait for a more detailed calculation.²²

In summary, the detailed optical properties of BaFe₂As₂ have been determined above and below $T_N \approx 138$ K. We have identified both symmetry-allowed infrared-active E_u modes at ~ 94 and 253 cm⁻¹ at 295 K. In agreement with earlier work, we observe a loss of spectral weight in the Drude component below T_N corresponding to an almost 80% decrease in the number of free carriers; this spectral weight is transferred to a midinfrared band. In addition, we note the anomalous behavior of the 253 cm⁻¹ mode which undergoes a discontinuous shift in frequency at T_N , and which doubles in intensity for $T \ll T_N$. While there are several possible mechanisms by which this increase in intensity might be achieved, it is likely that a change in the nature of the bonding between the Fe and As atoms due to orbital ordering below T_N alters the character of the atomic displacements, resulting in an increase in the net dipole moment.

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