The exciting discovery of superconductivity in the iron-arsenic (pnictide) compound LaFeAsO₁₋ₓFₓ with a high critical temperature¹ Tc = 26 K has generated a great deal of interest in this class of materials. Other rare-earth substitutions² quickly increased Tc above 50 K, and Tc'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 TN = 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 (Tc = 29 K) or chemical doping⁹–¹¹ (Tc = 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 Tc are considered with the strong interplay between the lattice and magnetism, it is likely that the superconducting pairing interaction is not phonon mediated.¹² ¹³ However, electron-phonon coupling may be present in the pnictides.¹³ ¹⁴ Optical investigations of the nonsuperconducting BaFe₂As₂ compound¹⁵ 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 observed²⁰ or if they have been observed,²¹ 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,²¹ 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 TN; this mode involves displacements in the Fe-As layer. The possible origins of this behavior are discussed, with the most compelling being a orbital-ordering scenario resulting in a change in the nature of the bonding.²² ²³

Large single crystals of BaFe₂As₂ were grown by a self-flux method.¹¹ The reflectance has been measured above and below TN 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 observed¹⁵ ¹⁶. As the temperature is reduced the low-frequency reflectance continues to increase, but for T < TN 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 TN = 312 K, and in the charge- and spin-stripe ordered state of La₂−xBaₓCuO₄ 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
The character of the conductivity changes dramatically with the temperature. Below \(T_N\), the real part of the optical conductivity in the low-frequency region for BaFe\(_2\)As\(_2\) for light polarized in the \(a\)-\(b\) planes for several temperatures above and below the structural and magnetic transition at \(T_N = 138\) K. Inset: the real part of the optical conductivity in the region of the infrared-active mode at \(\approx 253\) cm\(^{-1}\).

The spectral weight is defined simply as the weight under the optical conductivity curve over a given interval, \(\int_0^{\Omega} \sigma_j(\omega, T) d\omega\). 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 \(\approx 94\) 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\(_2\)As\(_2\) is in the tetragonal \(I4/mm\) space group. The irreducible vibrational representation in the high-temperature tetragonal (HTT) phase is\(^{29}\)

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

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

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

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, \textit{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 \(\Omega = 226\) to 315 cm\(^{-1}\), leading to a doubling in the intensity.

### 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 \(\omega_j\), \(\gamma_j\), and \(\Omega_j\) 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\(^{-1}\).

| \(\omega_j\) (meV) | \(\gamma_j\) (meV) | \(\Omega_j\) (meV) |
|------------------|------------------|------------------|
| 94.0 (0.1)       | 3.5 (0.4)        | 222 (8)          |
| 253.2 (0.1)      | 4.1 (0.2)        | 226 (7)          |
| 95.4 (0.2)       | 3.9 (0.9)        | 236 (17)         |
| 257.5 (0.1)      | 2.7 (0.2)        | 315 (8)          |

FIG. 2. (Color online) The real part of the optical conductivity in the low-frequency region for BaFe\(_2\)As\(_2\) for light polarized in the \(a\)-\(b\) planes for several temperatures above and below the structural and magnetic transition at \(T_N = 138\) K. Inset: the real part of the optical conductivity in the region of the infrared-active mode at \(\approx 253\) 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; however, in the cobalt-doped analog 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.

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. It is possible that below $T_N$ there might be a redistribution of charge. 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 BaFe$_2$As$_2$ 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 BaFe$_2$As$_2$ have been determined above and below $T_N$=138 K. We have identified both symmetry-allowed infrared-active $E_u$ modes at $\sim$94 and 253 cm$^{-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 $T< T_N$. 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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1Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
2Z.-A. Ren et al., EPL 82, 57002 (2008).
3W. Yi et al., EPL 84, 67009 (2008).
4M. Rotter, M. Tegel, D. Johrendt, I. Schellenberg, W. Hermes, and R. Pöttgen, Phys. Rev. B 78, 020503(R) (2008).
5X. F. Wang, T. Wu, G. Wu, H. Chen, Y. L. Xie, J. J. Ying, Y. J. Yan, R. H. Liu, and X. H. Chen, Phys. Rev. Lett. 102, 117005 (2009).
6C. de la Cruz et al., Nature (London) 453, 899 (2008).
7M. D. Johannes and I. I. Mazin, Phys. Rev. B 79, 220510(R) (2009).
8P. L. Alireza, Y. T. C. Ko, J. Gillett, C. M. Petrone, J. M. Cole, G. G. Lonzarich, and S. E. Sebastian, J. Phys.: Condens. Matter 21, 012208 (2009).
9M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. 101, 107006 (2008).
10K. Sasmal, B. Lv, B. Lorenz, A. M. Guloy, F. Chen, Y.-Y. Xue, and C.-W. Chu, Phys. Rev. Lett. 101, 107007 (2008).
11A. S. Sefat, R. Jin, M. A. McGuire, B. C. Sales, D. J. Singh, and D. Mandrus, Phys. Rev. Lett. 101, 117004 (2008).
12L. Boeri, O. V. Dolgov, and A. A. Golubov, Phys. Rev. Lett. 101, 026403 (2008).
13H. Eschrig, arXiv:0804.0186 (unpublished).
14M. L. Kulić and A. A. Haghighirad, EPL 87, 17007 (2009).
15W. Z. Hu, J. Dong, G. Li, Z. Li, P. Zheng, G. F. Chen, J. L. Luo, and N. L. Wang, Phys. Rev. Lett. 101, 257005 (2008).
16F. Pfunder, J. G. Analytis, J.-H. Chu, I. R. Fisher, and L. Degiorgi, Eur. Phys. J. B 67, 513 (2009).
17G. Li, W. Z. Hu, J. Dong, Z. Li, P. Zheng, G. F. Chen, J. L. Luo, and N. L. Wang, Phys. Rev. Lett. 101, 107004 (2008).
18J. Yang, D. Hühnchen, U. Nagel, T. Rööm, N. Ni, P. C. Canfield, S. L. Bud’ko, J. P. Carbotte, and T. Timusk, Phys. Rev. Lett. 102, 187003 (2009).
19J. J. Tu et al. (private communication).
20T. Shimojima et al., arXiv:0904.1632 (unpublished).
21Z. G. Chen, G. Xu, W. Z. Hu, X. D. Zhang, P. Zheng, G. F. Chen, J. L. Luo, Z. Fang, and N. L. Wang, Phys. Rev. B 80, 094506 (2009).
22W. Lv, J. Wu, and P. Phillips, arXiv:0905.1704 (unpublished).
23C.-C. Lee, W.-G. Yin, and W. Wu, arXiv:0905.2957 (unpublished).
24C. C. Homes, M. Reedyk, D. Crandles, and T. Timusk, Appl. Opt. 32, 2976 (1993).
25A. S. Barker, Jr. and J. A. Ditzenberger, Phys. Rev. B 1, 4378 (1970).
26C. C. Homes, S. V. Dordevic, G. D. Gu, Q. Li, T. Valla, and J. M. Tranquada, Phys. Rev. Lett. 96, 257002 (2006).
27T. Valla, A. V. Fedorov, J. Lee, J. C. Davis, and G. D. Gu, Science 314, 1914 (2006).
28M. A. Tanatar, N. Ni, G. D. Samolyuk, S. L. Bud’ko, P. C. Canfield, and R. Prozorov, Phys. Rev. B 79, 134528 (2009).
29A. P. Litvinchuk, V. G. Hadjiev, M. N. Iliev, B. Lv, A. M. Guloy, and C. W. Chu, Phys. Rev. B 78, 060503(R) (2008).
30T. Yildirim, Phys. Rev. Lett. 101, 057010 (2008).
31E. Dowty, Phys. Chem. Miner. 14, 67 (1987).
32U. Fano, Phys. Rev. 124, 1866 (1961).
33R. Bozio, M. Meneghetti, and C. Pecile, Phys. Rev. B 36, 7795 (1987).
34K.-Y. Choi, Y. G. Pashkevich, K. V. Lamonova, H. Kageyama, Y. Ueda, and P. Lemmens, Phys. Rev. B 68, 104418 (2003).
35C. C. Homes, A. W. McConnell, B. P. Clayman, D. A. Bonn, R. Liang, W. N. Hardy, M. Inoue, H. Negishi, P. Fournier, and R. L. Greene, Phys. Rev. Lett. 84, 5391 (2000).
36S. C. Zhao et al., Supercond. Sci. Technol. 22, 015017 (2009).
37K.-Y. Choi, D. Wulferding, P. Lemmens, N. Ni, S. L. Bud’ko, and P. C. Canfield, Phys. Rev. B 78, 212503 (2008).