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Optical conductivity of superconducting $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ single crystals: Evidence for a Josephson-coupled phase

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The optical properties of the iron-chalcogenide superconductor $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ with a critical temperature $T_c = 31$ K have been measured over a wide frequency range in the a - b planes above and below T_c . The conductivity is incoherent at room temperature, but becomes coherent (Drude-like) at $T \gtrsim T_c$; however, $R_\square \simeq 320$ k Ω , well above the threshold for the superconductor-insulator transition at $R_\square = h/4e^2 \simeq 6.9$ k Ω . Below T_c , the superfluid density $\rho_{s0} \simeq 48 \times 10^3$ cm $^{-2}$ places this material on the scaling line $\rho_{s0}/8 \simeq 4.4 \sigma_{dc} T_c$, but in a region associated with Josephson coupling, suggesting this material is inhomogeneous and constitutes a Josephson phase.

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The discovery of superconductivity in the iron-arsenic (pnictide) material $\text{LaFeAsO}_{1-x}\text{F}_x$ [1] and the rapid increase in the critical temperature T_c above 50 K through rare-earth substitutions [2], has prompted the search for related iron-based superconductors in the hope of achieving even higher values for T_c . While superconductivity was quickly discovered in $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$ [3] and the iron-chalcogenide $\text{FeTe}_{1-x}\text{Se}_x$ [4], the maximum value for T_c in these compounds is $\simeq 38$ and 15 K, respectively. In the iron-based superconductors, scattering between hole and electron pockets in this class of materials is considered a necessary element for high critical temperatures [5]. Indeed, in the KFe_2As_2 material, the electron pockets that are present in all the other iron-based materials are absent, leaving just the hole pockets at the center of the Brillouin zone and a severely reduced $T_c \simeq 3$ K [6, 7]. The discovery of superconductivity in $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ with $T_c \gtrsim 30$ K [8] was greeted with enthusiasm not only because of the relatively high value for T_c , but also as a result of its unique electronic structure. In this material the hole pockets at the center of the Brillouin zone are absent, leaving just the electron pockets at the edges of the zone [9–11]; however, the value for $T_c \simeq 30$ K is an order of magnitude larger than in the hole-doped analog, suggesting that the spin fluctuation pairing mechanism may have to be re-evaluated [12]. In the superconducting state $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ displays a nearly isotropic gap of 8 – 10 meV on the Fermi surfaces [9–11]. Evidence for phase separation and the coexistence of magnetism and superconductivity has been observed in recent optical work on $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$ [13] and the related $\text{Rb}_2\text{Fe}_4\text{Se}_5$ material [14]; this interpretation is consistent with other recent experiments [15–18].

In this Letter we present the detailed in-plane optical properties of single crystal of $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ ($T_c = 31$ K) in both the normal and superconducting state. At room temperature the optical properties are dominated by the infrared-active vibrations and other bound excitations; the free-carrier response is incoherent. As the temper-

ature is reduced a coherent, or Drude-like, response is observed just above T_c . Below T_c a weak superconducting response is observed allowing the superfluid density ρ_{s0} to be estimated. This material is observed to fall on the general scaling line for the cuprate superconductors, $\rho_{s0}/8 \simeq 4.4 \sigma_{dc} T_c$ [19], but in a region typically associated with the c -axis response where the superconducting response is due to Josephson coupling, suggesting that this material is indeed phase separated and constitutes a Josephson phase [20].

Large single crystals of $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ were grown using a vertical unidirectional solidification method. Pieces of potassium were added to precursor FeSe to form the nominal composition and then placed into an alumina crucible and sealed in a quartz tube; this tube was

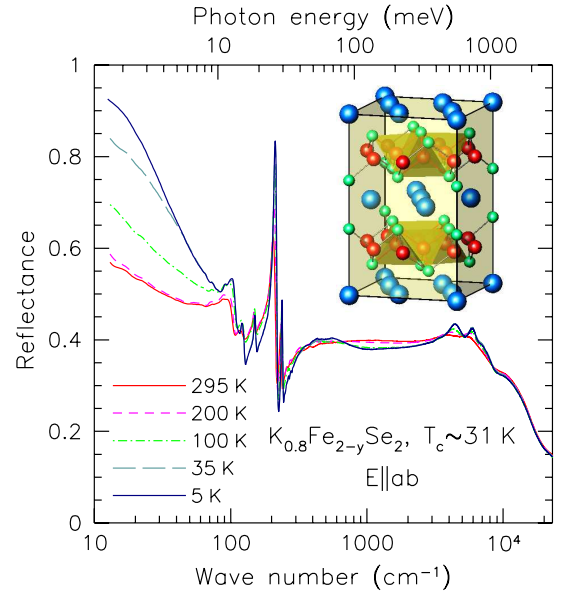


FIG. 1. The absolute reflectance over a wide frequency range for a cleaved single crystal of $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ for light polarized in the a - b planes at several temperatures above and below T_c . Inset: The unit cell in the $I4/m$ space group.

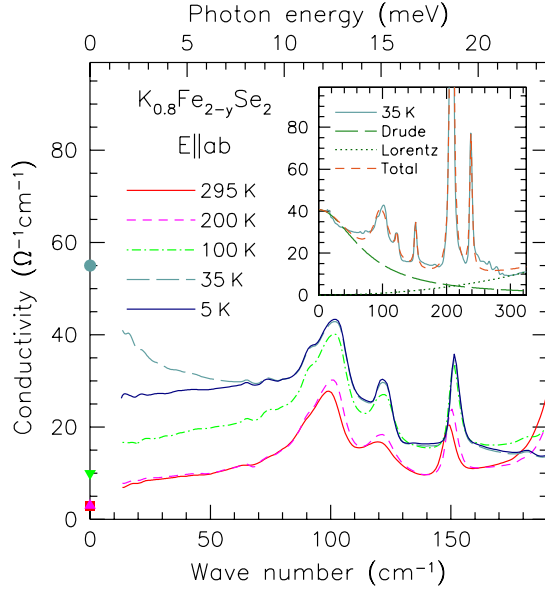


FIG. 2. The real part of the optical conductivity in the low-frequency region for $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ for light polarized in the a - b planes for several temperatures above and below $T_c = 31$ K. The polygons at the origin denote the values for the conductivity determined from transport measurements on a crystal from the same batch. Inset: Drude-Lorentz fit to the conductivity at 35 K.

then resealed in another quartz tube. This arrangement was heated to 1050°C and then cooled to 700°C , at which point the furnace was turned off and allowed to cool slowly to room temperature, yielding mm-sized single crystals. The room temperature resistivity of ~ 430 m Ω cm increases slightly upon cooling before beginning to decrease below about 250 K, reaching a value of about 18 m Ω cm just before the sample becomes superconducting at $T_c = 31$ K. The value for T_c has been determined from magnetic susceptibility. A single crystal of $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ approximately $2\text{ mm} \times 2\text{ mm} \times 100\text{ }\mu\text{m}$ was mounted on an optically-black cone and cleaved, revealing an mirror-like surface; the sample was immediately transferred to a cryostat and placed under vacuum. The reflectance for light polarized in the iron-selenide (a - b) planes has been measured using an *in-situ* overcoating technique [21] from the terahertz (1.5 meV) to the ultraviolet (~ 4 eV) region for a variety of temperatures above and below T_c , shown in Fig. 1. The relatively low value for the reflectance is characteristic of a poor metal and it is dominated by the infrared-active vibrations, as well as other electronic features at higher energy. The low-frequency reflectance initially displays little temperature dependence, but begins to increase rapidly below ~ 200 K, with an abrupt increase below T_c . The complicated electronic behavior contained in the reflectance may be seen more clearly in the optical conductivity, which is determined from a Kramers-Kronig analysis of

TABLE I. The fitted vibrational parameters for the in-plane infrared active lattice modes in the optical conductivity of $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ at 35 K, where ω_j , γ_j and Ω_j are the frequency, width and oscillator strength of the j th mode. The errors are estimated from the covariance and are indicated in parenthesis. All units are in cm^{-1} .

ω_j ($\delta\omega_j$)	γ_j ($\delta\gamma_j$)	Ω_j ($\delta\Omega_j$)
65.2 (0.2)	2.5 (0.3)	10 (2)
73.6 (0.2)	3.7 (0.4)	15 (3)
93.7 (0.2)	18.1 (3.4)	118 (17)
102.3 (0.6)	10.5 (0.9)	103 (17)
121.9 (0.6)	9.2 (0.8)	78 (6)
151.7 (0.3)	3.8 (0.5)	67 (6)
181.9 (0.3)	4.5 (0.2)	16 (2)
208.3 (0.1)	4.4 (0.1)	322 (8)
238.3 (0.1)	4.3 (0.2)	131 (6)
267.1 (0.2)	2.9 (0.2)	22 (3)
278.6 (0.2)	5.2 (0.2)	32 (3)

the reflectance [22].

The calculated conductivity is shown in the low-frequency region in Fig. 2. At room temperature the conductivity is dominated by a series of sharp features associated with the infrared-active lattice modes, superimposed on a flat, incoherent electronic background. As the temperature is reduced, the vibrational features narrow and increase slightly in frequency. Below ~ 200 K the low frequency conductivity begins to gradually increase, until just above T_c the response may be described 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, $\omega_{p,D}^2 = 4\pi ne^2/m^*$ and $1/\tau_D$ are the plasma frequency and scattering rate for the delocalized (Drude) carriers, respectively, and m^* is an effective mass tensor; ω_j , γ_j and Ω_j are the position, width, and oscillator strength of the j th vibration. The complex conductivity is $\tilde{\sigma}(\omega) = \sigma_1 + i\sigma_2 = -i\omega[\tilde{\epsilon}(\omega) - \epsilon_\infty]/4\pi$. The inset in Fig. 2 shows the result of a non-linear least-squares fit to the conductivity at 35 K using a single Drude component as well as a number of Lorentz oscillators to reproduce the narrow phonon features and the broader excitations observed at high frequency.

The large number of vibrations observed in this material (listed in Table I) is surprising given that in tetragonal BaFe_2As_2 ($I4/mmm$) only two in-plane infrared active E_u modes are expected and observed, and that even below the magnetic and structural transition the orthorhombic distortion ($Fmmm$) only yields an additional two modes [23], far fewer than observed here. However, it has been remarked that the $I4/m$ tetragonal unit cell for $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ (shown in the inset of Fig. 1) is larger and

more complicated than the related iron-arsenic structure [24–26]. We have determined the irreducible vibrational representation using the $I4/m$ space group,

$$\Gamma_{vib} = 9A_{1g} + 9B_{1g} + 9E_g + 7A_u + 7B_u + 10E_u.$$

The g modes are Raman active and the B_u modes are silent; only the A_u and E_u vibrations are infrared active along the c axis and in the a - b planes, respectively. The large number of infrared-active modes is in agreement with observation; however, while only 10 modes are predicted, a minimum of 11 modes are observed (two additional features, weak shoulders associated with the two strong modes at $\simeq 208$ and 238 cm^{-1} are difficult to fit and have not been included). This suggests that some of the observed modes may be due to a secondary phase, the activation of Raman modes due to disorder, or both.

In addition to the lattice modes, there are a number of broad features observed at high frequency, shown in Fig. 3. The prominent features at $\simeq 4600$, 5900 and 7100 cm^{-1} have been observed in optical studies of the K and Rb doped iron selenides [14, 27] and are labeled α , β and δ , respectively. We also observe an unusual low-energy feature at $\simeq 760$ cm^{-1} , denoted γ . The three high-frequency features are thought to be related to spin-controlled interband transitions [14, 27]. Given that the 760 cm^{-1} feature displays the same temperature dependence, it is possible that it may have a similar origin. The spectral weight associated with these features increases at low temperature; however, this is compensated by a decrease in adjacent regions so that the total spectral weight $N(\omega_c) = \int_0^{\omega_c} \sigma_1(\omega) d\omega$ is constant when ω_c is sufficiently large ($\omega_c \gtrsim 1.5$ eV).

The Drude parameters $\omega_{p,D} \simeq 430 \pm 20$ cm^{-1} and $1/\tau_D \simeq 70 \pm 5$ cm^{-1} determined from the fit to the optical conductivity at 35 K [28] reveal that the Drude plasma frequency is more than an order of magnitude smaller than what is observed in comparable iron-pnictide [29] or iron-chalcogenide materials [30]. A generalized-Drude model [31, 32] indicates that the enhancement of the effective mass at 35 K is rather small, $m^*(\omega \rightarrow 0)/m_e \simeq 2$. This corresponds to a dilute carrier concentration of $n \simeq 4 \times 10^{18}$ cm^{-3} , considerably less than the estimates based on NMR measurements [33]. Given the small value for n , it is reasonable to ask whether or not this material is homogeneous. Just above T_c we note that $\sigma_{dc} = \sigma_1(\omega \rightarrow 0) \simeq 44$ $\Omega^{-1}\text{cm}^{-1}$, or $\rho_{dc} \simeq 23$ $\text{m}\Omega\text{cm}$. The highly-anisotropic nature of these materials [34] suggests that the transport be described in terms of a sheet resistance $R_{\square} = \rho_{dc}/d$, where d is the separation between the iron-chalcogenide sheets. Using $d \simeq 7$ Å [24–26] yields $R_{\square} \simeq 320$ $\text{k}\Omega$. This value is significantly larger than the threshold for the superconductor-insulator transition [35] observed to occur close to $R_{\square} = h/4e^2 \simeq 6.9$ $\text{k}\Omega$, suggesting that this material may not be homogeneous.

Below T_c in the superconducting state the conductivity shows a characteristic suppression below $\simeq 65$ cm^{-1} .

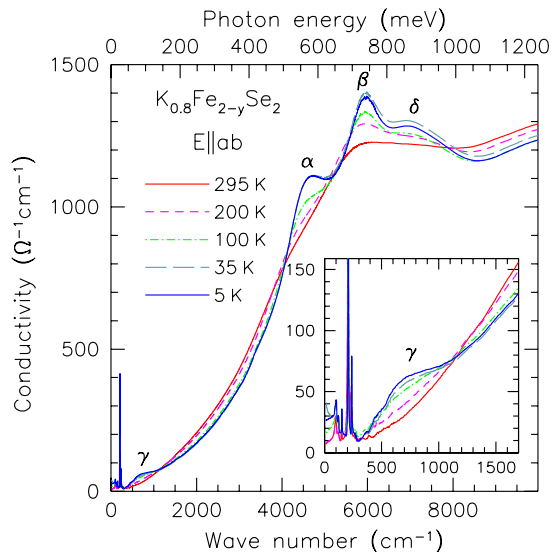


FIG. 3. The real part of the optical conductivity for light polarized in the a - b planes of $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ over a wide frequency range for several temperatures above and below T_c . Two previously observed features are labeled α and β ; two new features at low and high frequency are denoted as γ and δ , respectively. Inset: The detailed behavior of the γ feature.

The strength of the condensate may be determined from the Ferrell-Glover-Tinkham sum rule, $N(\omega_c, T \gtrsim T_c) - N(\omega_c, T \ll T_c) = \omega_{p,S}^2/8$, where $\omega_{p,S}$ is the superconducting plasma frequency and ω_c is a cut-off frequency, allowing the superfluid density $\rho_{s0} \equiv \omega_{p,S}^2$ to be calculated. The small value for the missing area, the large amount of residual conductivity, and the proximity to a number of phonon modes can all be significant sources of uncertainty for this sum rule. However, these difficulties can be overcome by using the alternative method $\omega_{p,S}^2 = \omega \sigma_2(\omega)$ in the $T \ll T_c$, $\omega \rightarrow 0$ limit [36]. The value $\omega_{p,S} \simeq 220 \pm 20$ cm^{-1} (yielding an effective penetration depth $\lambda_{eff} \simeq 7.2 \pm 0.7$ μm) is an order of magnitude smaller than what is observed in other iron-arsenic [29] and iron-chalcogenide [30] superconductors. It has been pointed out that a number of the iron-based superconductors fall on the scaling relation initially observed for the cuprate superconductors, $\rho_{s0}/8 \simeq 4.4 \sigma_{dc} T_c$ [19], shown in Fig. 4. The inhomogeneous nature of this material makes it difficult to associate a given value for σ_{dc} with the superconducting regions. If we consider the residual conductivity to originate mainly from a weakly-metallic component that does not contribute to superconductivity, then we can estimate $\sigma_{dc} \approx \sigma_1(T \gtrsim T_c) - \sigma_1(T \ll T_c) \simeq 18$ $\Omega^{-1}\text{cm}^{-1}$ in the $\omega \rightarrow 0$ limit; we attach the provision that there is a considerable amount of uncertainty associated with this estimate. Using these values, $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ does indeed fall on the scaling line in Fig. 4; however, it does so in a region associated with the response along the c axis in the

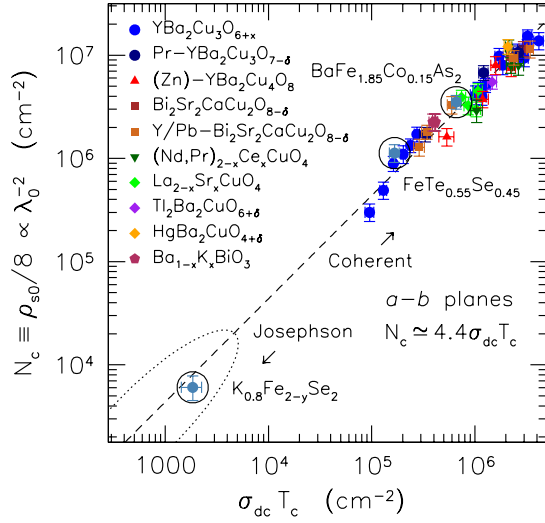


FIG. 4. The log-log plot of the spectral weight of the superfluid density $N_c \equiv \rho_{s0}/8$ vs $\sigma_{dc} T_c$ in the a - b planes for a variety of electron and hole-doped cuprates compared with $\text{BaFe}_{1.85}\text{Co}_{0.15}\text{As}_2$ [29], $\text{FeTe}_{0.55}\text{Se}_{0.45}$ [30], and $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ (this work), highlighted by the circles. The dashed line corresponds to the general result for the cuprates $\rho_{s0}/8 \simeq 4.4\sigma_{dc}T_c$, while the dotted line denotes the region of the scaling relation typically associated with Josephson coupling along the c axis.

cuprates where the superconductivity is due to Josephson coupling between the copper-oxygen planes. This is further evidence that the material is inhomogeneous and that it constitutes a Josephson phase, in agreement with other recent results [13–18]. While it is tempting to associate the decrease in the low-frequency conductivity below T_c with the formation of a superconducting energy gap $2\Delta \simeq 8$ meV, this value is significantly smaller than the ARPES estimates of $2\Delta \simeq 16$ meV [9–11]. Moreover, the previous statement that the superconductivity in this material is due to Josephson coupling implies that the energy scale for changes in the reflectance and conductivity should occur in the region of the renormalized superconducting plasma frequency, $\tilde{\omega}_{p,S} = \omega_{p,S}/\sqrt{\epsilon_{\text{FIR}}}$; allowing that $\omega_{p,S} \simeq 220$ cm^{-1} represents an average value for a distribution of frequencies [13] and given the experimentally-determined value $\epsilon_{\text{FIR}} \simeq 18$ at 50 meV, then $\tilde{\omega}_{p,S} \simeq 52$ cm^{-1} is reasonably close to the changes observed in the conductivity below about 65 cm^{-1} .

In summary, the in-plane optical conductivity of $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ ($T_c = 31$ K) is incoherent at room temperature where it is dominated by infrared-active lattice modes and other high-frequency bound excitations. Just above T_c a coherent, Drude-like, response emerges, but the fitted value $\omega_{p,D} \simeq 430$ cm^{-1} is quite small. Moreover, $R_{\square} \simeq 320$ k Ω at 35 K, well above the threshold for the superconductor-insulator transition observed at $R_{\square} = h/4e^2 \simeq 6.9$ k Ω . Below T_c the superconducting plasma frequency $\omega_{p,S} \simeq 220$ cm^{-1} is more than an order of magnitude smaller than what is observed in other iron-

based superconductors. This material falls on the scaling line $\rho_{s0}/8 \simeq 4.4\sigma_{dc}T_c$, but does so in a region associated with Josephson coupling along the poorly-conducting c axis in the cuprate superconductors. Taken together, the normal and superconducting state properties suggest an inhomogeneous, phase separated material, in which the superconductivity is due to Josephson coupling.

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