Electronic Correlations and Unconventional Spectral Weight Transfer in the High-Temperature Pnictide $BaFe_{2-x}Co_xAs_2$ Superconductor Using Infrared Spectroscopy

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We report an infrared optical study of the pnictide high-temperature superconductor $BaFe_{1.84}Co_{0.16}As_2$ and its parent compound $BaFe_2As_2$. We demonstrate that electronic correlations are moderately strong and do not change across the spin-density wave transition or with doping. By examining the energy scale and direction of spectral weight transfer, we argue that Hund's coupling J is the primary mechanism that gives rise to correlations.

Strongly correlated materials present some of the most interesting challenges to both experimental and theoretical physicists alike. A profound experimental manifestation of correlations is the renormalization of electronic bands due to interactions that are not included in the standard band theory description [1–3]. Correlations are well known to give rise to complex phase diagrams, as evidenced by the long-standing problem of high-temperature superconductivity in cuprates [4,5]. Since the discovery of the iron-pnictide superconductors, one pressing question in this field is whether correlations in general, and Mott physics specifically, are among necessary preconditions for the high-T_c phenomenon. While both the cuprates and pnictides exhibit an antiferromagnetically ordered ground state in proximity with the superconducting phase ([6,7], and references therein), the parent compounds of the iron-pnictide materials are metallic with striped spin-density wave order, unlike the antiferromagnetic Mott insulating cuprate parent compounds. As we will show for the 122 class of pnictides, the influence of magnetism via Hund's coupling is the predominant correlation mechanism and is crucial to the electronic properties of the paramagnetic normal and superconducting states.

We measured the optical reflectivity of the parent $BaFe_2As_2$ (Ba122) and optimally doped $BaFe_{1.84}Co_{0.16}As_2$ (Co-Ba122) compounds as a function of temperature over a broad spectral range and extracted the optical constants as described in [8]. The real part of the optical conductivity $\sigma_1(\omega)$ is plotted in Fig. 1. The following discussion will distinguish properties of the spin-density wave (SDW) state, which applies only to the parent compound for $T < T_{SDW} \approx 140$ K, from properties of the paramagnetic (PM) normal state, which applies to $T > T_{SDW}$ in Ba122 and $T > T_c$ in Co-Ba122. All of the $\sigma_1(\omega)$ spectra in the PM state involve a broad Drude response extending to at least

1500 cm^{-1}. In the SDW state, $\sigma_1(\omega)$ is dominated at low energy by the formation of the SDW gaps, exhibiting only a very narrow Drude response [9,10]. Doping does not seem to drastically alter $\sigma_1(\omega)$ in the PM state.

The renormalization of electronic bands due to correlations has a significant effect on two specific observables in infrared spectroscopy: One is a reduced oscillator strength of the Drude response compared with band theory predictions, and the other is the energy scale of spectral weight transfer. We now explore each of these observables in turn. (In [8], we present more details about the samples, experiment, and determination of the SDW gap values.)

In order to quantify the first observable, a reduction of the Drude response compared to band theory, we use a truncated version of the f-sum rule [1]. The experimental kinetic energy K_{exp} is proportional to the spectral weight of the Drude component of the optical response and is determined via an integral of the real part of the optical conductivity up to a cutoff value Ω:

$$K_{exp}(\Omega) = \frac{120}{\pi} \int_0^{\Omega} \sigma_1(\omega) d\omega. \qquad (1)$$

Here we have formulated the equation for kinetic energy in units of cm^{-2}. The cutoff value Ω should be high enough so as to account for all of the Drude weight yet not so high as to include significant contributions from interband transitions. The multiband character of the pnictides presents a caveat for this procedure, due to the potential for low-lying interband transitions. We then normalize K_{exp} to K_{LDA}, the band theory estimate under the local density approximation (LDA). The same procedure was used to explore correlations in several different families of exotic superconductors including the pnictides [1–3,11]. The ratio spans from the extremely correlated case of a fully localized Mott insulator (e.g., the cuprate parent compounds where
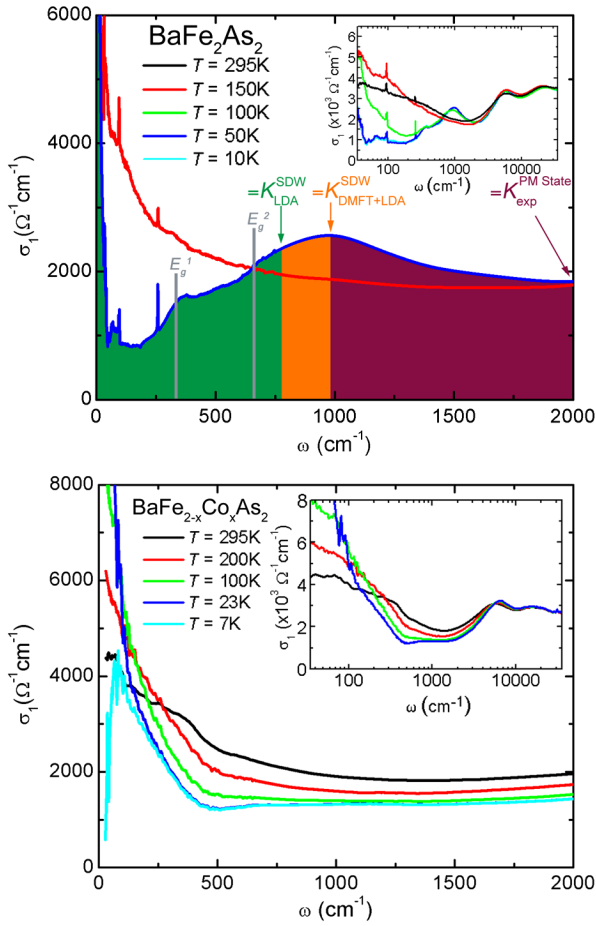
FIG. 1 (color online). Real part of the optical conductivity σ_1 in Ba122 (top) in the PM ($T = 150$ K) and SDW ($T = 50$ K) states and Co-Ba122 (bottom) in the PM normal state and superconducting state ($T = 7$ K). For Ba122, we illustrate the necessary integration cutoffs $\Omega = 777$, 969, and 2000 cm^{-1} in order to recover the predicted LDA, LDA + DMFT, and experimentally observed PM state kinetic energy values, respectively. The third cutoff demonstrates that the spectral weight transfer due to the SDW gaps extends to 2000 cm^{-1} and not above.

$K_{\exp}/K_{\text{LDA}} \approx 0$) to electronically uncorrelated materials such as a fully itinerant metal (e.g., copper where $K_{\exp}/K_{\text{LDA}} \approx 1$). The comparison is instructive, because band theory with LDA does not take into account Coulomb repulsion U or magnetic interactions that can renormalize the electronic bandwidth and consequently reduce the kinetic energy. Therefore, the ratio of $K_{\exp}/K_{\text{LDA}}$ emphasizes the significance of correlations due to processes beyond the band theory description.

In Figs. 2(a)–2(c), we plot $K_{\exp}/K_{\text{LDA}}$ as a function of the cutoff frequency, Ω. The LDA kinetic energy values are given in the caption and were obtained as described in a recent work by Yin, Haule, and Kotliar [12]. Using arrows, we point out the various cutoffs explained in Ref. [8]. Irrespective of the cutoff criteria, we find that, for Ba122, $K_{\exp}/K_{\text{LDA}} = 0.25$–0.29 in the PM and 0.2–0.34 in the
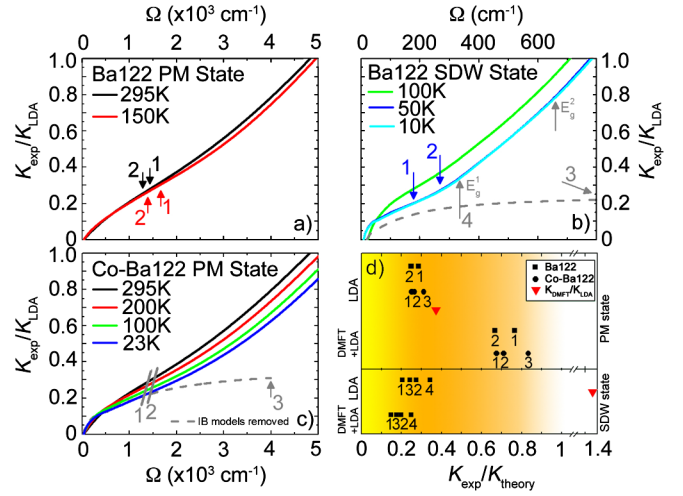

FIG. 2 (color online). (a)–(c) The kinetic energy ratio $K_{\exp}(\Omega)/K_{\text{LDA}}$ in Ba122 and Co-Ba122, as a function of integration cutoff value Ω [Eq. (1)]. The ratio for Ba122 in the PM (a) and SDW (b) states and for Co-Ba122 in the normal PM state (c). The numbers and arrows indicate the results of the four methods for determining the kinetic energy integration cutoff, described in [8]. (d) The temperature-averaged results of the kinetic energy ratio $K_{\exp}(\Omega)/K_{\text{theory}}$ in the PM and SDW states, compared with both LDA and LDA + DMFT results, including the theoretical kinetic energy values. The triangles show the value of the ratio of the two theoretical kinetic energies determined via LDA and LDA + DMFT in the PM and SDW states. The values from theory are $K_{\text{LDA}}^{\text{PM}} = (21\,133\ \text{cm}^{-1})^2$, $K_{\text{LDA}}^{\text{SDW}} = (6937\ \text{cm}^{-1})^2$, $K_{\text{DMFT}}^{\text{PM}} = (12\,905\ \text{cm}^{-1})^2$, and $K_{\text{DMFT}}^{\text{SDW}} = (8147\ \text{cm}^{-1})^2$.

SDW state. In Co-Ba122, we observe a similar value in the PM normal state: $K_{\exp}/K_{\text{LDA}} = 0.15$–0.31. Our results demonstrate that correlations are present in the PM state and remain unchanged at low temperature in the fully developed SDW state and with doping into the superconducting state.

One recent attempt to theoretically explain the optical conductivity and magnetic moment in the PM state of Ba122 utilizes dynamical mean field theory in conjunction with the local density approximation (LDA + DMFT) [12]. In Fig. 2(d), we have also plotted the ratio $K_{\exp}/K_{\text{DMFT}}$, where K_{DMFT} corresponds to the kinetic energy predicted by using LDA + DMFT. This theory can be understood to describe a PM metal with a fluctuating magnetic moment. In Ba122, we find that in the PM state $K_{\exp}/K_{\text{DMFT}} = 0.67$–0.77, while in Co-Ba122 the ratio is $K_{\exp}/K_{\text{DMFT}} = 0.68$–0.83. We therefore confirm the ability of LDA + DMFT to more accurately describe the optical response in the PM state. However, this conclusion does not hold for the SDW state. In fact, LDA + DMFT underestimates the degree of correlations by an extra 30% over LDA alone, giving $K_{\exp}/K_{\text{DMFT}} = 0.15$–0.25. This is surprising due to the qualitative agreement between our data and the theoretical spectra. (We note that this

discrepancy between K_{exp} and K_{DMFT} may be entirely explained by the excessively high background conductivity in the theoretical results [12].)

Comparison with theory allows us to determine that the strength of correlations in $BaFe_{2-x}Co_xAs_2$ is significant [$K_{exp}(\Omega)/K_{LDA} \approx 0.4$ is an upper bound; for a full description of the sources of error inherent within our technique, see [8]]. The strength is on a par with what is known to produce the highest T_c in optimally doped cuprates [1,2,11]. Such reduced kinetic energy from theoretical expectations implies that additional spectral weight (SW) is present at energies higher than the Drude response. In order to elucidate the mechanisms that drive correlations in the Ba122 pnictides, one must determine the energy scale associated with this SW. However, the higher energy SW contribution is not immediately evident in $\sigma_1(\omega)$ due to the obscuring presence of interband transitions. Similar complications arise with doped Mott insulators where the energy scale of U overlaps with the interband structure. Nevertheless, it is possible to gain direct information about the magnitude of U in doped Mott insulators by carefully monitoring the distribution of SW as it changes with doping and temperature [13,14]. We utilize this approach in the pnictides by monitoring the energy scale of SW transfer in $\sigma_1(\omega)$.

In Fig. 3, we plot the ratio of the integrated SW at low temperature $K_{exp}(T, \Omega)$ to the room temperature value $K_{exp}(295 \text{ K}, \Omega)$, where the cutoff value Ω extends throughout the entire measured frequency range. This ratio emphasizes the relevant energy scale of SW transfer. If there is a transfer of SW from high to low energy, the SW ratio will exceed 1 at low energy and then smoothly approach 1 until the full energy scale of the Drude oscillator is reached. If there is a transfer of SW from low to high energy, the SW ratio will fall below 1 until the total energy scale of SW transfer is reached.

We now discuss the SW ratios in the PM state (Fig. 3). As temperature decreases, the Drude response narrows and some SW shifts lower in energy. This is in accordance with expectations for a metal and causes the SW ratio to exceed 1 below $\approx 600 \text{ cm}^{-1}$. Yet between ≈ 600 and 8000 cm^{-1}, the ratios decrease to well below 1. There is a minimum in the PM state ratios near 3000 cm^{-1}, indicating a turning point in SW transfer: Below this value SW is depleted, while above this value SW is amassed. By $\approx 8000 \text{ cm}^{-1}$, the ratios return to ≈ 1 as all of the SW is recovered. Therefore, SW is transferred from the Drude response into the region between 3000 and 8000 cm^{-1} in both Ba122 and Co-Ba122. The energy scale of SW transfer is determined by observing the energy range over which most of the spectral weight is recovered, marked in Fig. 3 with vertical dashed lines. By this criterion, the energy scale for correlations in the PM state is $\approx 8000 \text{ cm}^{-1}$.

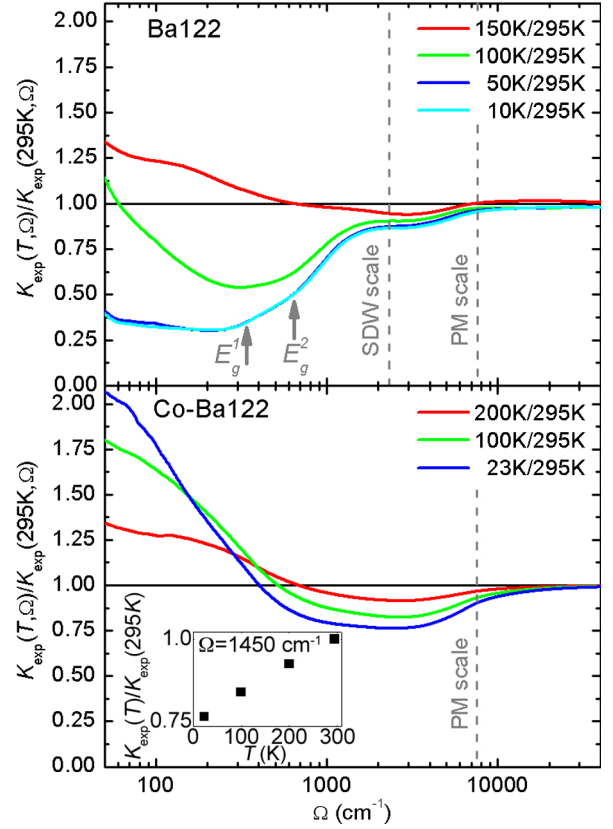In the SDW state in Ba122, we observe the superposition of two concomitant processes, each with its own energy

FIG. 3 (color online). Ratio of the integrated conductivity $K_{exp}(T, \Omega)/K_{exp}(295 \text{ K}, \Omega)$ as a function of cutoff value Ω and temperature over the entire measured frequency range in Ba122 (top panel) and Co-Ba122 (bottom panel). The ratios are taken with respect to the $T = 295$ K data in order to display the temperature evolution of the PM and SDW SW transfer. The two vertical dashed bars show the energy scale below which all of the SW transfer takes place, for both the PM and SDW states. The energy scale of SW transfer in the PM state is $\approx 8000 \text{ cm}^{-1}$ and in the SDW state is $\approx 2000 \text{ cm}^{-1}$. Inset: Temperature dependence of the kinetic energy of the Drude response, normalized to the room temperature value, at a cutoff $\Omega = 1450 \text{ cm}^{-1}$.

scale of SW transfer. The energy scale relevant for correlations in the PM state persists in the SDW state. In addition, there is SW transfer at lower energies, consistent with the formation of the SDW gaps. When the SDW state forms, a peak in $\sigma_1(\omega)$ emerges at finite frequency. Therefore, the SW in the remaining Drude response plus the SW in the SDW peak should be equal to the SW in the Drude response in the PM state. This is the case in Ba122, exemplified in Fig. 1 (top panel), where we show that, in order to recover SW equal to the Drude response in the PM state, the integration cutoff must be equal to the frequency where the SDW peak returns to the PM state value ($\Omega \approx 2000 \text{ cm}^{-1}$). Therefore, we contend that the SW transfer in the SDW state can be understood as a superposition of two processes: the gapping of states due to SDW order, restricted to energies below $\approx 2000 \text{ cm}^{-1}$, and SW transfer from low to high energy over the same energy

scale as in the PM state, extending to energies as high as ≈ 8000 cm^{-1}. This shows that the SDW state does not introduce additional electronic correlations in Ba122.

Having determined the energy scale of SW transfer, we are now in a position to compare our observations with the energy scales potentially relevant for correlations in the 122 materials: the Hubbard U and Hund's coupling J. The difference of the physical origin of these two processes is significant. In Mott-Hubbard systems, correlations result from reduced charge fluctuations, where double occupancy is highly penalized. In Hund's metals, the charge fluctuations are not much reduced, but the quasiparticles nevertheless can become strongly correlated, because electrons on the same Fe ion tend to form high spin due to Hund's rule coupling. For the system to become a Fermi liquid, this high spin needs to be screened by the electrons on the neighboring ions. Such large spin on Fe is very hard to screen by hopping between ions, resulting in strongly correlated quasiparticles.

Experimentally, x-ray absorption spectroscopy can directly access the magnitude of U and J. A recent work determined that, in Ba122, $U \leq 2$ eV $\approx 16\,000$ cm^{-1} and $J \approx 0.8$ eV ≈ 6400 cm^{-1} [15], while other x-ray absorption spectroscopy experiments determined, for a broad class of pnictides, that $U = 3$–4 eV $\approx 24\,000$–$32\,000$ cm^{-1} and $J \approx 0.8$ eV ≈ 6400 cm^{-1}, in agreement with constrained DFT calculations ([16] and references therein). In LDA + DMFT calculations, including those that produce an optical conductivity closely resembling our data [12], the interaction strengths ranged between $U = 3$–4 eV [16,17] and $U \gtrsim 5$ eV [18] and $J = 0.6$–0.9 eV ≈ 3600–7200 cm^{-1}. On the other hand, mean field theory results suggest an intermediate value of $U = 2$–4 eV [19], while a multi-orbital Hubbard model under the mean field approximation gives $U \approx 1.5$ eV and $J \approx 0.3$–0.6 eV [20].

All of these results point to a picture where $U \approx 2$–5 eV while J is some fraction thereof: $J \approx 0.6$–0.9 eV. Comparing the values of U and J with our SW data, it is clear that the Coulomb scale $U \approx 2$–5 eV is larger than the observed SW transfer in our samples [21], especially considering the fact that the bulk of the literature we reviewed leans towards the larger value of U within the above interval. Moreover, as demonstrated, SW does not significantly change with doping, while in a Mott insulator the effective number density of carriers increases linearly with doping.

Of additional importance is the *direction* of SW transfer. In most strongly correlated metals derived from Mott insulators, the Drude oscillator strength grows at lowered temperatures due to SW transfer from high to low energy, over an energy scale of the Hubbard $U/2$ [22]. (An example of this behavior can be found in the electronic response of V_2O_3 in the high-temperature metallic state [13,23].) SW transfer in the cuprates, while not universally true in the most underdoped compounds, is generally from

high to low energy with decreasing temperature, over an energy scale associated with U [24–27] (see [8] for more references and a detailed discussion of this point). Therefore, we find that, for systems where the Coulomb repulsion U defines the correlation scale, SW transfer is from high to low energy as temperature is decreased, resulting in a larger Drude response at low temperature. The situation in the 122 pnictides is quite different, where the SW transfer at low temperature is from *low to high* energy. As can be readily observed in the Fig. 3 inset, SW in the Drude response *decreases* as temperature is lowered [28–30]. Such behavior is reminiscent of doped semiconductors and sets the pnictides apart from correlated metals derived from Mott insulators.

By studying both the direction and energy scale of SW transfer, the evidence weighs in favor of a correlation mechanism predominantly due to Hund's coupling [31]: $J \approx 0.6$–0.9 eV, which is equal to the scale of SW transfer that we observe. These results are unexpected in light of doped Mott insulators such as the cuprates, where electronic correlations decrease as the material is doped. On the contrary, our observation of a constant kinetic energy ratio as a function of doping is evidence against a Mott-like correlation mechanism [1]. Moreover, unconventional SW transfer from low to high energy is also observed in P-doped and Co-overdoped Ba122, indicating that it may be a general phenomenon in the pnictides [32]. In the future, a systematic study of detwinned samples may reveal important anisotropies [33,34] of the SW transfer.

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