High energy pseudogap and its evolution with doping in Fe-based superconductors as revealed by optical spectroscopy

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Abstract

We report optical spectroscopic measurements on electron- and hole-doped BaFe$_2$As$_2$. We show that the compounds in the normal state are not simple metals. The optical conductivity spectra contain, in addition to the free carrier response at low frequency, a temperature-dependent gap-like suppression at fairly high energy scale near 0.6 eV. This suppression evolves with the As–Fe–As bond angle induced by electron or hole doping. Furthermore, the feature becomes much weaker in the Fe-chalcogenide compounds. We elaborate that the feature is mainly caused by the strong Hund’s rule coupling effect between the itinerant electrons and localized electron moment arising from the multiple Fe 3d orbitals. The coupling strength changes with the environment of the Fe atom. Our experiments demonstrate the coexistence of itinerant and localized electrons in iron-based compounds, which would then lead to a more comprehensive picture of the metallic magnetism in the materials.

(Some figures may appear in colour only in the online journal)

1. Introduction

The interplay between superconductivity and magnetism is one of the central topics in the study of Fe-based superconductors [1]. Similar to the high-$T_c$ cuprates, the superconductivity in Fe-based compounds is found to be in close proximity to an antiferromagnetic (AFM) order [2, 3]. Superconductivity emerges when the magnetic order was suppressed by electron or hole doping or application of pressure [2, 4–6]. Although the phase diagram of Fe pnictides looks very similar to that of high-$T_c$ cuprates, distinct differences exist between them. The undoped compounds in cuprates are Mott insulators; by contrast, the parent compounds in Fe pnictides/chalcogenides are multiband metals. The magnetic interaction effect also manifests in the paramagnetic phase. The uniform magnetic susceptibility $\chi$ in both parent compounds above $T_N$ and superconducting compounds above $T_c$ is neither Pauli- nor Curie–Weiss-like; instead, it increases linearly with increasing temperature within the measured temperature range [7]. Furthermore, the value of $\chi$ is roughly two orders larger than the value for Pauli paramagnetism. Many debates have been focused on whether the magnetism has an itinerant electron or local moment interaction origin, an issue that is intimately related to the pairing interaction for superconductivity.

The complex magnetic properties arise from the multiple orbital nature of the systems. The electronic structures of the multiple orbital systems should also be reflected in the charge excitation spectra which could be probed by the optical spectroscopy technique. Previous optical investigations on the parent compounds of AFe$_2$As$_2$ (A = Ba, Sr, Eu) [8–14] revealed clearly the formation of the partial energy gaps at low energy in the magnetic phase, indicating the involvement of the itinerant electrons in the spin-density-wave (SDW) order formation. Nevertheless, the gap opening at low energy is not the sole spectral feature observed with decreasing...
temperature. As indicated in the early study [8], there exists another remarkable temperature-dependent spectral feature at much higher energy scale. The spectral weight below $\sim 5000 \text{ cm}^{-1}$ (0.6 eV) is gradually suppressed with decreasing temperature and transfer to higher energy scale (see the grey region in figure 1). This suppression is observed even at room temperature. This pseudogap-like behaviour at such a high energy scale is not expected for an usual metal. Although most of the spectral weight at such a high energy scale comes from the interband transitions, the temperature-dependent part must have a different origin. It has been a long-standing mystery for the Fe-based compounds ever since the optical spectra were collected on single crystal samples [8].

In this work, we address this issue by examining the evolution of the high energy pseudogap with electron and hole dopings. We found that the feature remains strong in the electron-doped side, including the heavily electron-doped case where the compound is no longer superconducting, but it becomes much weaker in the heavily hole-doped case. Our analysis indicates that this high energy gap-like feature is closely related to the doping-induced crystal structural change, particularly the As–Fe–As bond angle, or the height of the As position relative to the Fe layers. We elaborate that the high energy feature is mainly caused by the strong intra-atomic Hund’s rule coupling effect due to the presence of multiple Fe 3d orbitals. Our study supports the coexistence of itinerant and localized electrons in Fe pnictides, which would then lead to a more comprehensive picture of the metallic magnetism in the materials.

2. Experiment

Single crystals of K- and Co-doped BaFe$_2$As$_2$ were grown from the FeAs flux method, similar to the procedure in our earlier report [15]. The plate-like crystals could be easily cleaved, resulting in a very shiny surface. We present four different samples: two K-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with $x = 0.4 \ (T_c = 37 \text{ K})$ and $x = 1 \ (T_c = 3 \text{ K})$, and two Co-doped BaFe$_{2-y}$Co$_y$As$_2$ with $y = 0.2 \ (T_c = 22 \text{ K})$ and $y = 0.4 \ (T_c = 37 \text{ K})$. We also compare the measurement data with the parent compounds BaFe$_2$As$_2$ and Fe$_{1.05}$Te. It is well known that the K$^+$ doping for Ba$^{2+}$ introduces extra holes. On the other hand, the NMR experiment indicated that Co$^{2+}$ doping for Fe$^{2+}$ does not induce local moment but gives one more d electron to the system, and therefore has the effect of electron doping [16]. Roughly, $T_c = 37$ and 22 K are close to the highest superconducting transition temperatures achieved by K doping (off the FeAs plane) and Co doping (within the FeAs plane), respectively, i.e. they are optimally doped. However, BaFe$_{1.6}$Co$_{0.4}$As$_2$ is heavily electron doped; by contrast, KFe$_2$As$_2$ is heavily hole doped. The phase diagram of the K- and Co-doped BaFe$_2$As$_2$ is shown in figure 2 [17, 18]. The studied compositions are indicated in the figure.

The optical reflectance measurements were performed on a combination of Bruker IFS 66/s, 113v on newly cleaved surfaces (ab plane) of those crystals up to 25 000 cm$^{-1}$. An in situ gold and aluminum overcoating technique was used to get the reflectivity $R(\omega)$. The real part of the conductivity $\sigma_1(\omega)$ is obtained by the Kramers–Kronig transformation of $R(\omega)$.

3. Results and discussion

Figure 3 shows the experimental reflectance and conductivity spectra for different samples. For a comparison, we also include the data of BaFe$_2$As$_2$ [8] and Fe$_{1.05}$Te [19] compounds. The low frequency data vary significantly for these samples because of the different ground states. Superconducting pairing energy gap features exist in the Co-doped (Co = 0.2) and K-doped (K = 0.4) superconducting samples at very low frequencies (not visible clearly in the plot over such a broad energy scale). Clear SDW gap features were seen for the pure BaFe$_2$As$_2$ sample. Purely metallic temperature-dependent responses were observed for the heavily electron- or hole-doped samples. But here we focus our attention on the high energy gap-like spectral weight suppression features. It deserves mention that optical studies on the Co-doped 122 samples at or below the optimal doping level have been reported previously [13, 20–24]; however, the high energy gap-like feature and its origin were not addressed.

In the optical reflectance spectrum $R(\omega)$, the high energy structure manifests itself as a suppression of $R(\omega)$ in the mid-infrared region (about 2000–5000 cm$^{-1}$). As the low-$\omega$ $R(\omega)$ still increases towards unity due to the metallic nature of the compounds, a reverse S-like shape in $R(\omega)$ results. In figure 3 we find that, compared to the parent BaFe$_2$As$_2$
Figure 3. The evolution of the optical spectra of BaFe$_2$As$_2$ with Co and K doping. Fe$_{1.05}$Te is added for comparison. Upper panel: $R(\omega)$ for the pure, Co- and K-doped BaFe$_2$As$_2$ and Fe$_{1.05}$Te up to 6000 cm$^{-1}$. Lower panel: $\sigma_1(\omega)$ for the pure, Co- and K-doped BaFe$_2$As$_2$ and Fe$_{1.05}$Te up to 8000 cm$^{-1}$.

Figure 4. The integrated spectral weight below 10 000 cm$^{-1}$ for BaFe$_2$As$_2$ [8] and BaFe$_{1.8}$Co$_{0.2}$As$_2$ single crystals. Insets display the plots of the spectral weight ratios at low temperature over that at high temperature.

compounds, the reverse S-like shape $R(\omega)$ remains fairly eminent in the Co-doped compounds. However, the feature becomes weaker in the $K = 0.4$ doped case, and tends to disappear in the pure KFe$_2$As$_2$ sample with a $T_c$ of only 3 K. The feature is also not visible in Fe$_{1.05}$Te.

Corresponding to the reverse S-like shape of $R(\omega)$, the real part of the conductivity $\sigma_1(\omega)$ shows a suppression roughly below 5000 cm$^{-1}$. This leads to a peak in $\sigma_1(\omega)$ near this energy, as shown in figure 3. Our earlier study on the parent compound indicated that the suppressed spectral weight is transferred to higher energies [8], indicating a pseudogap-like phenomenon.

To further elaborate on the spectral evolution, we plot the frequency-dependent spectral weight of $\sigma_1(\omega)$ at 10 and 300 K for two different crystals, the parent BaFe$_2$As$_2$ and Co-doped BaFe$_{1.4}$Co$_{0.6}$As$_2$, in figure 4. For the parent BaFe$_2$As$_2$, a residual Drude component exists in the SDW state. This residual Drude component narrows with decreasing temperature, and its low-frequency limit approaches the dc conductivity value. As a result, the low-$\omega$ spectral weight, roughly below 150 cm$^{-1}$, at low $T$ is higher than at high $T$. Above 150 cm$^{-1}$, the SDW gap develops, which strongly reduces the low-$T$ Drude weight, leading to the first suppression below 1000 cm$^{-1}$. The lost Drude weight fills into the SDW peak, and the total spectral weight is almost recovered around 2000 cm$^{-1}$ for 10 K. However, the $T$-dependent suppression below the mid-infrared peak results in the second spectral weight suppression at 10 K near 3000 cm$^{-1}$. The lost weight gradually recovers at very high energy, roughly 10 000 cm$^{-1}$. The above mentioned spectral features could be more clearly seen in the plot of the ratio of the spectral weight at 10 K over that at 300 K, as shown in the inset of the figure. The strong dip below 1000 cm$^{-1}$ represents the formation of the SDW gap. The second dip near 3000 cm$^{-1}$ reflects the development of the high energy pseudogap. For the Co-doped $x = 0.2$ crystal, there is no SDW gap that develops at low temperature; the low-$\omega$ spectral weight change is induced by the Drude component narrowing. A balance is seen near 1200 cm$^{-1}$. A further reduction of the spectral weight beyond this frequency at low temperature is caused by the gap-like suppression near 5000 cm$^{-1}$. Once again, these features could be seen clearly in the inset of the right panel of figure 4. The recovery of the spectral weight extends to fairly high energy scale. We should remark that, at such a high energy scale, most of the spectral weight would come from the interband transitions. However,
The temperature-dependent part must have a different origin. Seen clearly from figure 3, the pseudogap feature remains very strong for all Co-doped superconducting samples, but becomes weak in the K-doped compounds and tends to vanish for the pure KFe$_2$As$_2$. No suppression feature is visible in $\sigma_1(\omega)$ for Fe$_{1.05}$Te.

The key issue here is the origin of this high energy pseudogap. Unlike the spin-density-wave gap observed for the parent compounds only below magnetic ordering temperature, the high energy pseudogap feature is present at all measurement temperatures as well as in the doped compounds, as indicated in figure 3. Let us examine possible reasons for formation of a high energy peak structure.

One possibility is that the quasi-particles contain not only the coherent spectral weight at low energy but also the incoherent part at high energies due to the presence of a strong electron correlation effect [25–27]. The high energy feature comes from the incoherent part of the quasi-particle spectral function driven by the on-site Coulomb repulsion energy (Hubbard $U$). This should be a generic phenomenon for a strongly correlated electron system. A schematic picture of the quasi-particle spectral weight function is shown in figure 5. A dynamical mean-field theory calculation indicated that both the incoherent structures at intermediate frequencies of the order $U/2$ to $U$ and the coherent Drude component at the lower end of the conductivity spectrum rapidly emerge as the temperature is lowered [25, 26]. This has been used to explain the experimental observation of development of both Drude component and mid-infrared peak at low temperature in V$_3$O$_3$ [26]. However, this is different from the present case, where the Drude component already exists in Fe-based compounds at high temperatures. Furthermore, this picture is rather difficult to explain the doping evolution of the structure. In particular, Fe$_{1.05}$Te is believed to have stronger electron correlation, but the temperature-dependent feature in the mid-infrared is almost invisible. In fact, the conductivity spectrum in the mid-infrared region even has slightly lower values at lower temperature.

A different but related proposal is that the coherent spectrum at low frequency is due to the itinerant electrons from some Fe 3d orbitals which form the disconnected electron and hole Fermi surfaces, while the incoherent part is due to the Hubbard $U$ splitting of the localized bands from other Fe 3d orbitals [28, 29]. The occupation of the electrons in the lower Hubbard band results in the formation of local moments. In our opinion, this scenario also faces great challenges. The electron correlations in Fe-based compounds are not so strong. The band renormalization factors were found to be only about 2–3 [30–33]. Furthermore, some orbitals are almost degenerate. It is hard to image that these bands could be split by the relatively weak on-site electron correlation.

Because the feature is temperature dependent, one may argue that it is related to the spin fluctuations. A naïve idea is that the feature is caused by the indirect interband transitions assisted by the spin fluctuations with an AFM $(\pi, \pi)$ wavevector. As shown schematically in figure 6, the hole and electron bands are well connected by such a commensurate wavevector $q = (\pi, \pi)$ in the BaFe$_2$As$_2$ parent compound. The indirect interband transition could be realized through the assistance of $(\pi, \pi)$ spin fluctuations with the transition energy of $h\nu = E_F - E_i + \Omega$, where $E_i$ and $E_F$ are the energy levels of the initial and final states of the particle hole excitations, $\Omega$ is the energy corresponding to the formation of fluctuated AFM correlation which usually have a rather small energy scale. However, a careful examination indicates that this possibility is also unlikely. First, the bands close to the $\Gamma$ and M points are better connected by the $(\pi, \pi)$ wavevector; the lower energy region is expected to have higher indirect interband transition spectral weight with decreasing temperature, which is opposite to the suppression spectral feature at lower frequencies. Second, the opposite trend between electron and hole dopings strongly suggests against this scenario. The $(\pi, \pi)$ spin fluctuations are believed to be strongly suppressed in either heavily electron- or hole-doped compounds. Then, it is difficult to understand why the feature becomes weak only in the K-doped case but remains very strong in the Co-doped compounds.
To understand the first question, we have to assume that the kinetic energies of the electrons in different Fe 3d bands/orbitals are relatively close. Some may be slightly larger than the Hund’s coupling energy, while others may be slightly smaller than the Hund’s coupling energy. In other words, the energy levels or bands that contribute to the local moments are fairly close to the Fermi level where itinerant electrons dominate, so that the temperature change could affect their interaction. Indeed, the first principle band structure calculations on LaFeAsO and Ba122 indicated that all five orbitals of Fe 3d electrons are fairly close in energy [33]. The local moments estimated from the density function calculations are usually higher than 2 $\mu_B$, suggesting that more than two electrons are effectively localized, which contribute to the local moments. The situation is somewhat similar to the element $\alpha$-Fe, which has been known for several decades for the presence of both itinerant and localized d electrons. It deserves mention that recent neutron [42, 43] and Fe x-ray emission spectroscopy [44] experiments revealed the presence of large local moments in both parent compounds above $T_N$ and doped superconducting compounds above $T_c$.

An important observation in the present work is that the spectral weight transfer feature changes with doping, particularly in the K-doped case. From the crystal structural characterization, it is found that the K doping results in a continuous decrease of the $a$-axis parameter. More detailed analysis indicates that K doping does not induce detectable change in the Fe–As bonding length, but leads to a continuous decrease of As–Fe–As angle (the $\alpha$ angle in figure 7(b)) [18]. Equivalently, the height of the As atom relative to the Fe layer, $z$, is increasing. The Te height relative to the Fe layer in FeTe is further increased compared to Fe pnictides [38]. In contrast, the Co doping does not lead to an detectable change in the $a$-axis lattice parameter but only a slight decrease of $c$-axis parameter [45]. According to the band structural calculations, the band structure is rather sensitive to the As height relative to the Fe layer [39, 38, 40]. The increase of As height mainly makes the Fe atom more isolated, leading to a narrowing of the Fe 3d bands. As a result, the effective Hund’s coupling is enhanced [38]. Then the spectral weight suppression feature could not be seen within a temperature range change from 300 to 10 K. Higher temperature range would be required in order to see the spectral weight transfer structure. We found that the picture could well explain the evolution and the disappearance of the feature in Fe$_{1.05}$Te.

Finally, we comment on the spin-density-wave gap formation on the Fe pnictide compounds. Based on the above study, the local moment formation itself is not due to the Fermi surface nesting, but caused by the strong Hund’s coupling between different Fe 3d orbitals. However, the Fermi surfaces couple strongly with the magnetic instability. A spin-density-wave gap would open once the nesting of the Fermi surface’s matches with the magnetic wavevector.

4. Summary

In conclusion, our measurement indicates that the FeAs compounds are not simple itinerant electron systems. The
optical data of the 122 parent compound and their evolution with K and Co doping revealed spectral change not only at low but also considerably high frequencies. The spectral structure and its evolution implies the presence of both itinerant and localized electrons arising from different Fe 3d orbitals. We elaborate that the spectral weight transfer over the broad energies is related to the Hund’s coupling between itinerant and localized electrons. The coupling effect could be strongly affected by the environment of the Fe atom, i.e. the bonding angle of As–Fe–As or the height of As atom relative to the Fe layer. Our experiments demonstrate the coexistence of itinerant and localized electrons in iron-based compounds, which would then lead to a more comprehensive picture of the metallic magnetism in the materials.

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Note added. After we completed this work, we noticed a recent optical work by Schafgans et al also pointing out the importance of Hund’s coupling in pnictides and chalcogenides from the spectral weight analysis [46].

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