Optical and Raman spectroscopy studies on Fe-based superconductors

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Abstract

A brief review of optical and Raman studies on the Fe-based superconductors is given, with special emphasis on the competing phenomenon in this system. Optical investigations on ReFeAsO (Re=rare-earth element) and AFe\textsubscript{2}As\textsubscript{2} (A=alkaline-earth metal) families provide clear evidence for the gap formation in the broken symmetry states, including the partial gaps in the spin-density wave states of parent compounds, and the pairing gaps in the superconducting states for doped compounds. Especially, the superconducting gap has an s-wave pairing lineshape in hole-doped BaFe\textsubscript{2}As\textsubscript{2}. Optical phonons at zone center detected by Raman and infrared techniques are classified for several Fe-based compounds. Related issues, such as the electron-phonon coupling and the effect of spin-density wave and superconducting transitions on phonons, are also discussed. Meanwhile, open questions including the T-dependent mid-infrared peak at 0.6-0.7 eV, electronic correlation, and the similarities/differences between high-T\textsubscript{c} cuprates and Fe-based superconductors are also briefly discussed. Important results from other experimental probes are compared with optical data to better understand the spin-density wave properties, the superconductivity, and the multi-band character in Fe-based compounds.

Key words: spin-density waves, superconductivity, iron pnictides, infrared and Raman spectroscopy

PACS: 78.20.-e, 78.30.-j, 75.30.Fv, 74.25.Gz, 74.25.Kc

1. Introduction

A new family of high temperature superconductors containing FeAs layers has attracted a broad interest since the discovery of superconductivity in LaFeAsO\textsubscript{1−}\textsubscript{x}F\textsubscript{x} (x=0.05−0.12) with T\textsubscript{c}=26 K by Kamihara \textit{et al.}\textsuperscript{[1]} When replacing the La ion by other rare-earth elements (Ce, Nd, Pr, Sm), T\textsubscript{c} could be raised to 40−55 K.\textsuperscript{[2,3,4]} In analogy with the high-T\textsubscript{c} cuprates, those quaternary oxy pnictides adopt a layered structure with the Fe\textsubscript{2}As\textsubscript{2} tetrahedron as an essential structural unit, in which the superconductivity appears when the antiferromagnetic ordering for this Fe-layer is suppressed by doping. However, unlike the cuprates where the undoped parent compounds are antiferromagnetic Mott insulators, the ReFeAsO (Re=La, Ce, Nd, Pr, Sm, etc.) parent compounds are metals or semimetals. The magnetic phase for the Fe-based parent compounds is identified as a spin-density wave (SDW) ordering.\textsuperscript{[5,6]}

Although the first FeAs superconductors are found on doped variants of ReFeAsO, it is soon reported that superconductivity could be induced in other types of structure containing the same tetrahedrally coordinated Fe\textsubscript{2}As\textsubscript{2} (or Fe\textsubscript{2}Se\textsubscript{2}) layers as in ReFeAsO compounds. Those include the oxygen-free AFe\textsubscript{2}As\textsubscript{2} (A=Ca, Sr, Ba, Eu) (122-type)\textsuperscript{[7,8,9,10,11,12,13,14,15,16]}, FeSe(Te) (11-type)\textsuperscript{[17,18]} and Li,FeAs (111-type)\textsuperscript{[19,20,21]}. Up to now, many of research works have been done on 122-type materials. This is because high-quality single crystals with sufficient sizes for different measurements could be easily grown for this type of Fe-based compounds, although their maximum T\textsubscript{c} does not exceed 38 K.

Optical and Raman spectroscopies are powerful experimental techniques in determining the charge dynamics and phonon response for solids. In this article, we briefly summarize current progress in optical and Raman spectroscopic studies, including the normal state properties, the SDW partial gap and superconducting gap, electronic correlation, and phonon spectra for Fe-based compounds. Comprehensive overviews on various physical properties for the superconducting Fe-based compounds could be found in this special issue on pnictide superconductors or in a recent review article by Sadovskii.\textsuperscript{[22]}

In the early stage, infrared spectroscopic studies on polycrystalline Fe-based compounds provide primitive information for the energy gaps in the broken symmetry states. The SDW partial gap is evidenced as a spectral suppression in the far-infrared for LaFeAsO, with a metallic response near the low frequency limit.\textsuperscript{[5,6]} Optical signature of the superconducting gap is also observed in superconducting ReFeAsO\textsubscript{1−}\textsubscript{x}F\textsubscript{x} polycrystals.\textsuperscript{[22,23]} When high-quality single crystalline AFe\textsubscript{2}As\textsubscript{2} becomes available, convinced spectroscopic evidence are obtained for the in-plane charge dynamics. Direct observation of the SDW partial gap in AFe\textsubscript{2}As\textsubscript{2}, and the s-wave symmetry of superconducting gap in Ba\textsubscript{0.8}K\textsubscript{0.2}Fe\textsubscript{2}As\textsubscript{2} are reported.\textsuperscript{[23,26]} Optical evidence for the s-wave superconducting gap indicates that the newly discovered Fe-based superconductor is apparently distinguishable from the high-T\textsubscript{c} cuprates.
More interestingly, both the SDW gap in parent compounds and the superconducting gap in the doped superconductors show a double-gap character for $\text{AFe}_2\text{As}_2$-type compound, reflecting the multi-band property in Fe-based system. Spectroscopic studies on single crystalline 122- and 1111-type Fe-based superconductors suggest the electronic correlation is moderate, with a possible electron-boson coupling signature in the optical quasiparticle self-energy, but the scattering rate $1/\tau(\omega)$ shows apparently different response to that of high-$T_c$ cuprates. A 0.6-0.7 eV mid-infrared feature is observed for both ReFeAsO and $\text{AFe}_2\text{As}_2$ systems, with a spectral weight redistribution to higher energies as decreasing $T$. Whether this high energy feature is a pseudogap or just an interband transition remains an open question.

The resistivity and free-carrier concentration of iron-based superconductors and their parent compounds are comparable to those of cuprates, which can be estimated by the published transport, Hall and infrared measurements and first-principle calculations. However, both experiments and theoretical calculations indicate that the Fe-based compounds show multi-band structures of $d$-orbitals, which can effectively increase the itinerancy of electrons and decrease electronic correlation. Consequently this would lead to a relatively enhanced Coulomb screening, which may raise the difficulties in searching for electronic Raman scattering signals. As we know, electronic Raman scattering detects density-density correlation in the charge channel. So far, studies on the zone center optical phonons obtain consistent results, while the ratio of signal to noise is low in Raman measurements compared to the case of cuprates. Raman and infrared active modes are investigated in combination with first-principle calculations. Compatible results are obtained by different groups. Raman, inelastic X-ray scattering measurements, and isotope effect experiments etc. provide important clues on the electron-phonon coupling in the Fe-based materials. Considering the similarities between the antiferromagnetic state in cuprates and the SDW state in the parent compounds of iron-based superconductors, it will be very interesting to explore if some magnetic excitations similar to twomagnon process can be observed by inelastic light scattering. Unfortunately, no such magnetic Raman scattering is reported at present.

2. Spin-density wave in the parent compound

An important progress in understanding the FeAs-based compounds is the identification of the SDW order in the parent compound. As we shall explain, essential information was obtained from the infrared spectroscopy measurement.

2.1. SDW in ReFeAsO

The FeAs-based system shows an interesting competing phenomenon. As shown in Fig. [1] the undoped LaFeAsO compound itself is not superconducting, but shows a strong anomaly near 150 K, below which the resistivity drops steeply. With fluorine doping, the anomaly shifts to lower temperature, and gradually disappears, then superconducting transition occurs.

Apparently, superconductivity competes with the phase showing the anomaly in this system. The anomaly was already observed in the earliest report by Kamihara et al. [11], however its origin was not addressed there. The first work of identifying the nature of this anomaly was done by Dong et al. in a combined experimental studies of transport/optical properties and first-principle band structure calculations. [5] Dong et al. found a very clear specific heat jump from specific heat measurement, suggesting that the anomaly is a second-order phase transition. Furthermore, the electronic specific heat coefficient determined at low temperature, $γ_{\text{el}}=3.7 \text{ mJ/mol K}^2$, is significantly smaller than the value obtained from the band structure calculations (about 5.5-6.5 mJ/mol K$^2$). Such a discrepancy is unconventional, because the band structure calculation usually gives a smaller value than the experimental data, and their difference is ascribed to the renormalization effect. Here a natural explanation for a larger theoretically predicted value is that a partial energy gap opens, which removes parts of the density of states below the phase transition temperature. This is indeed seen in their optical spectroscopy experiments on the parent compound.

Figure [2] shows the far-infrared reflectivity $\sigma(\omega)$ and conductivity $\sigma(\omega)$ for polycrystalline LaFeAsO. [5] Regardless of the five phonon modes in the far-infrared, one can find the reflectance is strongly suppressed below 600 cm$^{-1}$ at low temperature. This leads to a loss of low-frequency spectral weight in the real part of conductivity $\sigma(\omega)$ as shown in Fig. [2]. In fact, the $\sigma(\omega)$ already shows a weak suppression at 140 K, which becomes more apparent as decreasing temperature. A spectral suppression in the free-carrier contribution indicates a reduction of itinerant carriers, thus is an optical evidence for the energy gap on the Fermi surface. As the reflectance at very low frequency increases fast and exceeds the values at high temperature, the compound is still metallic even below the phase transition, being consistent with the enhanced $\text{dc}$ conductivity. The data indicate clearly that the Fermi surfaces are only partially gapped.

Identification of a gap formation below the phase transition strongly suggests that the anomaly is caused by a symmetry-
Conclusive evidence for the spin-density wave order is obtained from neutron experiments. Clarina de la Cruz et al. performed neutron diffraction measurement on LaFeAsO and demonstrated that an antiferromagnetic ordering develops at low temperature. In particular, the spin structure determined by their neutron experiment is identical to the spin configuration predicted based on the nesting of hole and electron Fermi surfaces proposed by Dong et al. However, the neutron experiments also revealed a very subtle structural distortion near 150 K, which accounts for the resistivity anomaly, while a magnetic ordering develops at a slightly lower temperature for LaFeAsO polycrystal. It is now widely believed that the structural distortion is driven by the magnetic instability.

Optical reflectance investigations were also carried out on other 1111-type polycrystalline parent compounds. Shortly after the work on LaFeAsO$_{1-x}$F$_x$, Chen et al. used the rare-earth element Ce to replace La and synthesize a series of CeFeAsO$_{1-x}$F$_x$ compounds. Interestingly, in this rare-earth based 1111 compound, a much higher $T_c$ ($41$ K) is achieved. From transport and optical spectroscopy measurement they identified very similar competing phenomena between spin-density wave and superconductivity in CeFeAsO$_{1-x}$F$_x$. Neutron experiment also revealed a stripe type antiferromagnetic order of the Fe sublattice in the parent compound, being identical to the LaFeAsO compound. The similarity between La- and Ce-based compounds suggest that the interplay between the superconductivity and the spin-density wave instability is a common phenomenon for FeAs-based systems. Additionally Chen et al. found that the Ce 4f electrons form local moments and ordered antiferromagnetically below 4 K, which coexists with superconductivity in CeFeAsO$_{1-x}$F$_x$.

The optical suppression (i.e., the SDW gap) is found for different types of ReFeAsO samples, however, as the optical data are collected on polycrystals, the $R(\omega)$ is dominated by several strong phonon modes related to the weakly conducting c-axis response. In particular, a strong oxygen-derived phonon mode around 438 cm$^{-1}$ weakens the ab-plane charge dynamics, it is therefore difficult to accurately define the energy scale affected by the SDW gap. Boris et al. report an infrared ellipsometry study on polycrystalline LaFeAsO parent compound and 10% F-doped superconductor LaFeAsO$_{1-x}$F$_x$, and found that the SDW-induced suppression in the optical conductivity $\sigma_1(\omega)$ has a rather large energy scale. Figure 3 shows the optical conductivity for both the parent and the F-doped samples. There is a low energy feature around 0.16 eV in LaFeAsO ($\omega_{PG}$ in Fig. 3), and the $\sigma_1(\omega)$ for 10 K is suppressed below that of 300 K for $\omega < \omega_{PG}$. This 0.16 eV feature disappears in the superconducting compound (Fig. 4). As F-doping suppress the antiferromagnetic transition, the 0.16 eV feature in LaFeAsO should be the SDW gap for the parent compound. Our published data on LaFeAsO only show the spectra below 700 cm$^{-1}$ (see Fig. 2), it is not clear whether the energy scope for the SDW-gap induced suppression extends to higher energies. In our latter study on another LaFeAsO polycrystal with higher quality (Fig. 4), the optical suppression indeed extend towards high frequency region, in agreement with the energy scale of 0.16 eV observed by Boris et al.
2.2. SDW in AFe$_2$As$_2$

After numerous attempts in Re-site chemical substitution for ReFeAsO, the maximum $T_c$ for this 1111-family is still below 56 K. Therefore, finding new structures containing the FeAs layer becomes the central task in materials research. ThCr$_2$Si$_2$-type compound AFe$_2$As$_2$ (A=Ba, Sr, Eu) is one of the important findings in the exploration for new types of Fe-based compound.[7] Figure 4 compares the optical reflectivity for polycrystalline LaFeAsO and EuFe$_2$As$_2$ ($T_{SDW}=190$ K).[37] One can find the spectral suppression related to SDW partial gap has a larger energy scale for EuFe$_2$As$_2$ than LaFeAsO. This could be due to the higher SDW transition temperature for EuFe$_2$As$_2$. In addition, the overall $R(\omega)$ for EuFe$_2$As$_2$ is substantially higher than that of LaFeAsO, suggesting a larger optical conductivity for EuFe$_2$As$_2$. Furthermore, only one weak phonon mode around 262 cm$^{-1}$ is seen in EuFe$_2$As$_2$, indicating screening from the conducting carriers is much better in the 122 system.

The discovery of superconductivity in hole doped ternary iron arsenide (Ba,K)Fe$_2$As$_2$[8] immediately attracts considerable interest in this 122 system.[9, 10, 11, 12, 13, 14] Benefited from high-quality single crystals, optical studies on the 122-type compounds achieve more profound progress than that in the 1111 system. A detailed optical study on single-crystal samples of BaFe$_2$As$_2$ and SrFe$_2$As$_2$ parent compounds was reported by Hu et al.[25] In this report, a double-gap character was found for both compounds, along with a dramatic reduction for the free-carrier spectral weight and scattering rate below $T_{SDW}$.

2.2.1. SDW double-gap

Figure 5 demonstrates the low frequency optical conductivity for BaFe$_2$As$_2$ ($T_{SDW}=138$ K) and SrFe$_2$As$_2$ ($T_{SDW}=200$ K). The Drude-like conductivity is seen at high temperature. However, a severe suppression of the Drude component is seen at low temperature, and the lost spectral weight gradually piles up into the absorption peaks at higher energies, suggesting a large amount of density of states are removed from $E_F$ by the energy gap for $T<T_{SDW}$. Interestingly, a double-peak structure is seen in the conductivity spectra. Considering the multi-band property for AFe$_2$As$_2$,[38] the double peaks in $\sigma_1(\omega)$ should correspond to two SDW gaps on separated Fermi surfaces. Here we note the absorption peaks in $\sigma_1(\omega)$ develop just below $T_{SDW}$, and the gap-like peaks no longer exist in the nonmagnetic state. Even for 205 K, which is just 5 K above the $T_{SDW}$ in SrFe$_2$As$_2$, no gap signature can be found. Therefore, the fluctuation effect for the SDW should be rather weak in AFe$_2$As$_2$. From the gap values and SDW transition temperatures, we obtained the ratio of $2\Delta/k_BT_{SDW}$ $\approx$3.5-3.6 for the smaller gap, and 9-9.6 for the larger gap for the two compounds. The smaller gap coincides roughly with the gap value expected by the conventional BCS relation, while the large one is very different.

Because of the presence of two different gap values in the SDW ordered state, direct information on where the FS sheets are gapped is highly desired. Several angle resolved photoemission spectroscopy (ARPES) investigations on AFe$_2$As$_2$ (A=Ba, Sr, Eu) report another gap-like feature around 0.65 eV and LaFeAsO.[36] Meanwhile, there is a significant spectral weight transfer for the parent and F-doped compounds. In LaFeAsO, the spectral weight redistribution associated with the pseudogap at 0.65 eV is restricted below 2 eV; while for superconducting LaFeAsO$_{0.9}F_{0.1}$, a substantial spectral weight transfer from below 2 eV to above 4 eV with increasing temperature is observed.[36]
or Sr) single crystals have been reported, however, two earlier works by Yang et al. [39] and Liu et al. [40] reported complete absence of SDW gaps, in sharp contrast to the infrared spectroscopy result. Very recently, Hsieh et al. report an orbital resolved ARPES study on SrFe$_2$As$_2$, and find evidence for an anisotropic SDW gap with energy scales on the order of 50 meV, which thus tends to be consistent with optical results. [41]

2.2.2. Free-carrier response

It is well-known that the low-$\omega$ Drude component comes from the itinerant carrier contribution. The Drude spectral weight determines the $\omega_p^2$ ($\omega_p$ is the plasma frequency), which is proportional to $n/m_{\text{eff}}$ (where $n$ is the carrier density, $m_{\text{eff}}$ is the effective mass); while its width reflects the carrier scattering rate $1/\tau$. As shown in Fig. 5 Drude components are present not only at $T>T_{SDW}$, but also in the SDW state below the gap-induced absorption peaks. Therefore, the Fermi surface of AFe$_2$As$_2$ is only partially gapped below $T_{SDW}$. Using a Drude-Lorentz fit, [42] we can extract the free-carrier contribution from $\sigma_1(\omega)$. The room $T$ plasma frequency is 12900 cm$^{-1}$ for BaFe$_2$As$_2$, and 13840 cm$^{-1}$ for SrFe$_2$As$_2$. Although the plasma frequency is larger than 1.5 eV, one should also note the scattering rate for the normal state is rather large, i.e., 700 cm$^{-1}$ for BaFe$_2$As$_2$ and 950 cm$^{-1}$ for SrFe$_2$As$_2$. Such a large scattering rate corresponds to an overdamped plasma edge in $R(\omega)$. [25] Below the SDW transition, both the plasma frequency and the scattering rate are dramatically reduced. The variations of $1/\tau$ and $\omega_p^2$ with temperature for the Drude term are shown in the insets of Fig. 5. Both parameters are normalized to their 300 K value. Provided the effective mass of itinerant carriers does not change with temperature, then the residual carrier density is only 12% of that at high temperature for both compounds. This means that roughly 88% of FS is removed by the gapping associated with SDW transitions. On the other hand, the scattering rate was reduced by about 92-96%. Therefore, the opening of the SDW partial gap strongly reduces the scattering channel, leading to a metallic behavior with enhanced dc conductivity in the gapped state. In the quantum oscillation measurement on SrFe$_2$As$_2$ single crystal, a large reduction of the paramagnetic Fermi surface by SDW transition is also observed, then the remaining Fermi surface pockets are only 2% of the original Brillouin zone area in the low $T$ phase. [43]

It should be remarked that the driving mechanism for the SDW instability in the parent compound is currently under debate. Although the stripe- or collinear-type antiferromagnetic order in the SDW state was first suggested to result from the nesting between the hole and electron Fermi surfaces (FS) of itinerant electrons, [5] it was alternatively proposed that the superexchange interaction of Fe ions mediated through the off-plane As atom plays a key role in the spin configuration formation. [27, 28, 29, 30, 44, 45] A stripe-type AFM would arise when the superexchange interaction between next-nearest-neighbor Fe sites becomes larger than half of the nearest neighbor exchange interaction. The optical study of Hu et al. shed light on this debating issue. Their data clearly demonstrate that the parent compounds are metallic both above and below SDW ordering temperatures. They have relatively high plasma frequency (a bit higher than 1.5 eV) in the normal phase. Furthermore, the partial gap values below SDW ordering temperatures are consistent with the expectation of nesting scenario where the temperature dependence of the gap should resemble that of BCS theory. Therefore, Hu’s work further favors the itinerant picture for the SDW instability. [5] Under such an itinerant picture, superconductivity in the doped system is mediated by spin fluctuation. [46, 47] where a sign reversal of the order parameters between different Fermi surfaces is obtained.

Figure 5: The real part of conductivity $\sigma_1(\omega)$ for (a) BaFe$_2$As$_2$ and (b) SrFe$_2$As$_2$ below 2500 cm$^{-1}$. The Drude term (short dash green line) and the first two Lorentz peaks abstracted from a Drude-Lorentz fit for $T=10$ K is shown at the bottom. Inset: normalized $1/\tau$ (black) and $\omega_p^2$ (blue). [25]

Figure 6: The spectral weight for BaFe$_2$As$_2$ below 10000 cm$^{-1}$. Inset: $\sigma_1(\omega)$ below 10000 cm$^{-1}$ (together with the low-$\omega$ extrapolation based on the dc conductivity). [25]
2.2.3. High energy feature

As mentioned above, Boris et al. observe a high energy pseudogap around 0.65 eV for LaFeAsO and LaFeAsO$_{0.95}$F$_{0.1}$ (Fig. 3), here similar T-dependent feature around 5000 cm$^{-1}$ (0.62 eV) also exists in BaFe$_2$As$_2$ and SrFe$_2$As$_2$. Figure 6 is the spectral weight analysis for BaFe$_2$As$_2$, from which two characteristic energy scales can be found: the first one below 2000 cm$^{-1}$ and the second one above 2000 cm$^{-1}$ up to 10000 cm$^{-1}$. In the first range ($\omega \lesssim 2000$ cm$^{-1}$), the narrowing of the Drude peak and the development of the SDW double-gap in the mid-infrared lead to a spectral weight redistribution from the free-carrier contribution into the gap induced absorption peaks as decreasing $T$ (see the conductivity data in Fig. 5 for comparison). This redistribution process is not complete until 2000 cm$^{-1}$, which is an energy scale related with the SDW gap. In the second range (2000-10000 cm$^{-1}$), there is another T-dependent spectral weight transfer from low to high energies due to the 5000 cm$^{-1}$ peak in $\sigma_1(\omega)$. This feature does not directly related with $T_{SDW}$ as it exists even in the non-magnetic state. As shown in the inset of Fig. 6, the 5000 cm$^{-1}$ mid-infrared peak dominates the conductivity spectrum for 300 K, which slightly moves towards higher energies for $T=10$ K. Correspondingly, the low frequency spectral weight also shifts towards higher frequencies at low $T$, and the total spectral weight recovers to normal-state value near 9000 cm$^{-1}$ (Fig. 6).

Similar mid-infrared component has been observed in the doped sample, e.g., (Ba,K)Fe$_2$As$_2$[26] and Ba(Fe,Co)$_2$As$_2$, and the temperature evolution for this 5000 cm$^{-1}$ peak seems unchanged in these doped systems. Such a high energy feature suggests the incoherent part for Fe 3d bands. Strictly speaking, one can not tell whether it is an interband transition or a pseudogap based on current optical data. Anyhow, here we note that a strong band renormalization in the 122-type compounds is found from recent ARPES studies.[41, 48, 49, 50, 51, 52] Therefore, the energy scales for possible interband transitions calculated from the LDA (local-density approximation) might deviate from experimental observation. The origin of this mid-infrared feature requires further studies.

2.3. Absence of the SDW gap for Fe$_{1+y}$Te

As shown above, the SDW gap induced suppression can be found for both ReFeAsO and AFe$_2$As$_2$. However, the 11-type single crystalline Fe$_{1.05}$Te, which undergoes a structural distortion along with the establishment of a long range antiferromagnetic order near 65K,[53, 54] shows no clear signature of the SDW gap.

Superconductivity with transition temperature $T_c$ up to 15 K was obtained on Fe$_{1+y}$(Se,Te) system at ambient pressure.[55-57] The $T_c$ can go up to 27 K at a pressure of 1.48 GPa.[58] Figure 7 shows the reflectivity $R(\omega)$ and the real part of conductivity $\sigma_1(\omega)$ for Fe$_{1.05}$Te.[59] The normal state reflectivity is similar to AFe$_2$As$_2$[25] that $R(\omega)$ has an almost linear frequency dependence up to mid-infrared region. It is important to note that the conductivity spectra above $T_{SDW}$ are rather flat. Definitely, it is not a semiconductor as no semiconductor-like gap could be found in $\sigma_1(\omega)$, but it is not a simple metal as well, because of the absence of a Drude-like peak. As is well known, the width of Drude peak is determined by the scattering rate (or inverse of the transport lifetime) of the quasiparticle, the measurement result indicates that there is no well defined quasiparticle. The origin of this mid-infrared feature requires further studies.

3. Superconductivity in the doped compound

Probing the energy scale and the symmetry of the superconducting gap are always important tasks for infrared spectroscopy. In the early stage, when only 1111-type polycrystals are available, the superconducting gap was observed as an abrupt increase of reflectivity in LaFeAsO$_{1-x}$F$_x$.[23] Soon, the superconducting gap in (Nd,Sm)FeAsO$_{0.85}$F$_{0.15}$ polycrystals were found by infrared ellipsometry.[24] In addition, a pronounced dip at 20 meV was found in the reflectivity ratio $R(\omega,T<T_c)/R(\omega,T_n)$ from a series Fe-doped SmO$_{1-x}$F$_x$FeAs polycrystals with unpolished surfaces.[62] The electron-phonon coupling was estimated by Drechsler et al. based on optical data collected on powder LaFeAsO$_{0.6}$F$_{0.4}$ and reported value of in-plane penetration depth.[63] With the availability of single crystalline samples of (A,K)Fe$_2$As$_2$ (A=Sr, Ba), more reliable in-plane optical data were obtained. The first optical evidence for an s-wave superconducting gap was found in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$[26] where the in-plane $R(\omega)$ suddenly turns up and approaches unity below $T_c$, following the well-established BCS description.
3.1. Probing the superconducting gap

Three length scales characterize the electrodynamics of superconductors, i.e., the London penetration depth $\lambda_L$, the correlation length $\xi_0$, and the mean free path of the uncondensed electrons $l$. The London penetration depth $\lambda_L = c/\omega_p$, where $\omega_p$ is the plasma frequency for the condensed carriers. The correlation depth is a characteristic scale within which the external magnetic field is exponentially screened. The correlation length $\xi_0$ is the spatial extension of the Cooper pairs. For superconductors, the dirty limit is the case in which $l \ll \xi_0$, thus the width of the Drude term $1/\tau$ in the normal state should be larger than the superconducting gap $2\Delta$; while the clean limit is a case that $l \gg \xi_0$, thus $1/\tau \ll 2\Delta$. The dirty limit and the clean limit can be distinguished by their different spectral responses. In the dirty limit, no clear signature of the superconducting gap could be found in $\sigma^\prime(\omega)$, because the spectral weight for the superconducting condensate lies below $2\Delta$, so that there is no detectable change of spectrum at the gap energy $2\Delta$ across the $T_c$. In the dirty limit, the normal-state Drude term is broader than $2\Delta$, therefore the disappearance of single-particle excitation below $2\Delta$ would lead an incoherent contribution in $\sigma^\prime(\omega)$, and the normalized spectral weight of the superconducting condensate converges much more slowly than in the clean-limit case. According to the optical sum rule\[42\] $\sigma^\prime(\omega) d\omega = \omega^2/8$, the area under $\sigma^\prime(\omega)$ should be conserved, and the total spectral weight is determined by the effective carrier density as the plasma frequency $\omega_p^2 = 4\pi N e^2/m^*$. In this sense, the lost spectral weight in $\sigma^\prime(\omega)$ below $T_c$ (so-called “missing area”) is a more essential character than the gap in optical spectrum.\[64\]

The “missing area” denotes the existence of superconducting condensate, i.e., a collective excitation at zero frequency with the form of $\delta(\omega)$ function. Using Kramers-Kronig relation, a term $\sigma^\prime(\omega) = A\delta(\omega)$ corresponds to $\sigma^\prime(\omega) = 2\Delta/\pi \omega$. Comparing with the London equation $\sigma^\prime(\omega) = c^2/4\pi l^2 \omega$, the penetration depth $\lambda$ calculated from the imaginary part of conductivity should be equal to that calculated from the “missing area” $\lambda$ in the real part of conductivity.\[64\]

\[
\lambda = c/\sqrt{8\Delta}
\]  

(1)

which is the famous Ferrell-Glover-Tinkham (FGT) sum rule.\[67\] As the imaginary part of the conductivity $\sigma^\prime(\omega)$ diverges as $1/\omega$ below $2\Delta$, it can be shown that the optical reflectivity $R(\omega)$ would rapidly approach to unity below the gap energy for BCS superconductor.\[42\] Therefore, the up-turn in $R(\omega)$ at low frequency for $T<T_c$ is an optical evidence for the superconducting gap, and a rapid saturation of reflectivity indicates the gap is isotropic (s-wave). While for the case of non-s-wave pairing, the optical reflectivity will slowly increases towards unity instead of an abrupt jump.

3.2. Superconducting gap in 1111-type polycrystal

The first optical investigation for the superconducting gap in FeAs-based superconductor was done on a LaFeAsO$_{1-x}$F$_x$ polycrystal. Transport measurements testify the existence of superconducting transition, and the ac magnetic susceptibility drops at 20 K.\[23\] Although the spectral change from 29 K to 20 K is hard to resolve in Fig. 8 an evident up-turn for $T=8$ K below 50–60 cm$^{-1}$ can be found (see the arrow in Fig. 8). Since the up-turn in optical reflectivity $R(\omega)$ corresponds to the onset energy of the superconducting gap, then $2\Delta/k_B T_c$ is 3.5-4.2 for LaFeAsO$_{1-x}$F$_x$ polycrystal, which is quite close to the prediction by BCS theory. Unlike the conventional BCS-type superconductor, here the reflectivity for LaFeAsO$_{1-x}$F$_x$ does not abruptly approach unity below $2\Delta$, but gradually increases towards the 100% line. A continuous increase in $R(\omega)$ is a common feature for high-$T_c$ cuprate where the superconducting gap has a d-wave symmetry.\[69\] However, no conclusion on the gap symmetry could be drawn from optical data on polycrystalline sample.

Further optical evidence for the superconducting gap in Fe-based superconductor is obtained from ellipsometric spectroscopy on polycrystalline NdFeAsO$_{0.82}$F$_{0.18}$ ($T_c=52$ K) and SmFeAsO$_{0.82}$F$_{0.18}$ ($T_c=45$ K).\[24\] Figure 9 shows the optical conductivity for NdFeAsO$_{0.82}$F$_{0.18}$ polycrystal at selected temperatures. The optical conductivity is dominated by four pronounced phonon modes in the far-infrared region for all temperatures. Regardless of these phonon modes, one can find the $T$-evolution for $\sigma^\prime(\omega)$ is changed across $T_c$: the $\sigma^\prime(\omega)$ is slightly enhanced due to the metallic response above $T_c$; while an obvious gap-like suppression below 300 cm$^{-1}$ could be found for $T<T_c$. The suppression can be more clearly resolved by the “missing area” in $\sigma^\prime(\omega)$. Figure 9 shows the difference spectrum $\sigma^\prime(10K)-\sigma^\prime(55K)$ as a function of frequency, and the inset plots the $T$-dependent spectral weight between 50 and 300 cm$^{-1}$. Dubroka et al. defines the superconducting gap $2\Delta$ as the onset energy for the optical suppression $\omega^*_{SC}$ (300 cm$^{-1}$ $\sim$ 37 meV), thus $2\Delta/k_B T_c$ $\approx$8.

As shown above, optical signatures of the superconducting gap are found in polycrystalline LaFeAsO$_{1-x}$F$_x$, SmFeAsO$_{1-x}$F$_x$, and NdFeAsO$_{1-x}$F$_x$. However, both methods used in Fig. 8 and 9 to identify the gap onset energy are not accurate. The pronounced phonon mode near 100 cm$^{-1}$ strongly affects the low frequency reflectivity, thus it is difficult to distinguish the exact frequency for the up-turn in $R(\omega)$. While subtracting the normal state spectra to cancel out the phonon information and using $\omega^*_{SC}$ (Fig. 9) as the gap will overestimate...
the gap in the dirty-limit. Then spectroscopic data on the single crystals are highly desirable.

### 3.3. Superconducting gap in 122-type single crystal

The first optical data on superconducting Ba$_{1-x}$K$_x$Fe$_2$As$_2$ single crystals were reported individually by two groups. Li et al. gave evidence for an s-wave superconducting gap in optimally doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$, and found the Ferrell-Glover-Tinkham sum rule was satisfied within an energy scale of 6Δ. Yang et al. studied the optical properties of Ba$_{0.55}$K$_{0.45}$Fe$_2$As$_2$ above its superconducting transition temperature (28 K), and concentrated on the normal state properties.

Figure 10 shows the ab-plane optical reflectivity for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ (T$_c$ = 37 K). The R(ω) for all T>T$_c$ follow a linear frequency dependence. When T<T$_c$, the R(ω) suddenly turns up below 300 cm$^{-1}$ and approaches unity around 150 cm$^{-1}$, which is a typical character for an s-wave superconducting gap. The temperature dependence of the optical conductivity is shown in Fig. 11. The Drude component narrows as decreasing T from 300 K to 45 K. For T<T$_c$, a large amount of the Drude weight in σ$_1$(ω) collapse into the superconducting condensate at zero frequency, leading to a non-zero excitation above 2Δ, and a "missing area" between 10 K and 45 K (see the inset figure). As shown in Section 3.1, the "missing area" in σ$_1$(ω) corresponds to the zero-frequency collective mode. The penetration depth estimated from the missing area is 2080 Å. The same quantity calculated from the imaginary part of optical conductivity σ$_\omega$(ω)=e$^2$/4πλ$^2$ω is λ=1950 Å. The good agreement for the penetration depth by different calculations indicated the validity of FGT sum rule in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. An inspection of the inset of Fig. 11 reveals that the "missing area" extends to the frequency roughly below 600 cm$^{-1}$, about 3 times larger than the higher superconducting energy gap 2Δ. This indicates that the superconducting condensate forms rapidly or the FGT sum rule is rapidly recovered. This is very different from underdoped high-T$_c$ cuprates where recovery of the FGT sum rule goes to very high energy, or the FGT sum rule is even violated.

According to the BCS theory in the dirty limit, there is no optical excitation for hω<2Δ, while above 2Δ the optical conductivity σ$_1$(ω) gradually rises due to the case II coherence factor. Since the σ$_1$(ω) for ω<2Δ is condensed into the zero frequency collective mode, σ$_\omega$(ω) will diverge as 1/ω for ω<2Δ, then a peak at 2Δ could be found in R(ω,T<T$_c$)/R(ω,T>T$_c$). As shown in Fig. 11 the conductivity is almost zero below roughly 150 cm$^{-1}$ due to the flat and
close to unity $R(\omega)$, which is an optical evidence for the s-wave superconducting energy gap. However, the peak in $R(\omega, 10 \text{ K})/R(\omega, 45 \text{ K})$ is around 200 cm$^{-1}$, thus yields a different energy scale for the superconducting gap. According to recent ARPES study on Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ (where the single crystalline sample comes from the same batch as the one used in optical study [26]), two isotropic gaps ($\Delta_1 \approx 6$–$8$ meV, $\Delta_2 \approx 10$–$12$ meV) are found on different Fermi surfaces [73,74,75]. Thus the discrepancy in the gap energies from $\sigma_1(\omega)$ and $R(\omega)/R_n$ might also suggest a two-gap character for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$.

### 3.4. Coherence factor and the double-gap in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$

Single electron transitions, induced by external perturbations such as electromagnetic radiation, ultrasound, or nuclear relaxation are determined by coherence factors, in addition to density of state effects. [76] Considering the transition rate $\alpha_s$ between energy levels $E$ and $E' = E + \hbar \omega$,

$$\alpha_s = \int |M|^2 F(\Delta, E, E') N_s(E) N_s(E')[f(E) - f(E')]dE$$

where $M$ is the magnitude of the one-electron matrix element thus $|M|^2$ the transition probability, $\Delta$ the single particle gap, $N_s(E)$ the density of states, $f(E)$ the Fermi distribution function $1/(1 + e^{(E - E_f)/k_B T})$, and $F(\Delta, E, E')$ the coherence factor. As shown by Tinkham [64] and Grünert [76], the electromagnetic absorption process for the density-wave and BCS superconducting ground states have different coherence factors since they are invariant under different symmetry operations. Thus,

$$\frac{\sigma^S_1}{\sigma^P_1} = \frac{1}{\hbar \omega} \int_{-\infty}^{\infty} \frac{|E(E + \hbar \omega) - \Delta^2| [f(E) - f(E + \hbar \omega)]}{(E^2 - \Delta^2)^{1/2}} dE$$

where $\sigma^S_1$ is the conductivity for the density-wave or superconducting state, $\sigma^P_1$ the conductivity for the normal state, and the upper sign corresponds to case I (e.g., SDW) and the lower to case II (e.g., BCS superconductor). Calculation for the conductivity ratio based on Eq. 3 requires numerical integration. However, the integral has a simple expression in terms of complete elliptic integrals for $T = 0 \text{ K}$. [64] The inset of Fig. 13 shows the calculation result based on Eq. 3 for the single-gap case. For the SDW ground state with an isotropic gap (case I), $\sigma^S_1/\sigma^P_1$ shows an asymmetry peak at the gap energy $2\Delta$, while for a BCS superconductor (case II) $\sigma^S_1/\sigma^P_1$ increases gradually above $2\Delta$. As $T/T_c$ (or $T/T_{SDW}$) appears in the exponent factor $(1/\exp(\Delta/k_B T))$ for numerical integration, deviation from the $T = 0 \text{ K}$ case can be neglected when $T \ll T_c$ (or $T \ll T_{SDW}$). The calculation can be further extended into the multiple-gap case, for instance, two BCS gaps on different Fermi surfaces. Model calculation for the two-gap case has been done by Barabash and Stroud [77].

Figure 13 shows the normalized optical conductivity $\sigma^S_1/\sigma^P_1$ in the broken symmetry state for two 122-type single crystals (the SDW state for BaFe$_2$As$_2$ parent compound and the superconducting state for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$). Different from the single-gap case as shown in the inset of Fig. 13 the optical conductivity for BaFe$_2$As$_2$ has a double-peak character with two energy scales ($\Delta_1 \equiv 2\Delta_{min}$ and $\Delta_2 \approx 2\Delta_1$). In addition, both peaks in $\sigma^S_1/\sigma^P_1$ for BaFe$_2$As$_2$ deviate from the very sharp peak from theoretical calculation of the isotropic gap as shown in the inset figure. Even for the lowest temperature $T = 10 \text{ K}$, the double peaks are still rather broad and round in shape, then one can hardly fit these experimental data by two isotropic gaps with the case I coherence factor. This could be in part attributed to the very complicated band structure with only partially gapped Fermi surfaces in the SDW ordered state.

Similar to the SDW double-gap in the parent compound, the superconducting Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ also shows a double-gap character after a normalization process for the optical conductivity (the onset of the second gap is marked by the arrow). As shown below, here the symmetry of the superconducting gap is s-wave. Using a two-gap model ($\Delta_1 = 7$ meV and $\Delta_2 = 12$ meV), we can reasonably reproduce the experimental data, while the calculation for a single gap at 7 meV shows larger discrepancy in the low frequency region (Fig. 14). Then one could find that the onset of optical excitation is determined by the smaller gap, but the fine structure in $\sigma_1(\omega)$ and the characteristic energy scale in $R(\omega)/R_n$ are dependent on the larger gap. Since the two-component s-wave gap function can well reproduce...
then comparable with that on electron doping, and the superconducting gap in $K$ superconductor, in which the magnetic transition at high temperature. A recent study on ReFePO based compounds, LaFePO does not have the antiferromagnetic has been successfully synthesized. Unlike the FeAs-1111-type compound from which relatively large single crystals are covered by Hosono’s group in 2006. It is also the first 4.1. Electron-boson coupling in LaFePO

LaFePO is the first superconducting Fe-based compound discovered by Hosono’s group in 2006. It is also the first 1111-type compound from which relatively large single crystal has been successfully synthesized. Unlike the FeAs-based compounds, LaFePO does not have the antiferromagnetic transition at high temperature. A recent study on ReFePO (Re=La, Pr, Nd) single crystals finds a different $T_c$ evolution that $T_c$ decreases as Ln is varied from La to Sm for ReFePO but increases for ReFeAsO$_{1-x}$F$_x$. In addition, a linear $T$-dependence for the penetration depth is found for LaFePO, suggesting a different superconducting mechanism in FeP- and FeAs-based superconductors. However, as large single crystalline 1111-type FeAs-based superconductor is still unavailable at present, spectroscopic study on LaFePO is useful to understanding the normal state properties for the Fe-based parent compound. Recent ARPES investigation indicates the ground state for LaFePO is itinerant, with no low-energy kink and no pseudogap for the bands near $E_F$, thus is clearly distinguishable from copper oxide superconductors.

Although the ARPES study does not find any low-energy kink for LaFePO single crystal, there is an optical evidence for a 62 meV electron-boson coupling mode in the optical quasiparticle self-energy. From Qazilbash et al.’s data, the Drude term in $\sigma_1(\omega)$ is well separated from the high energy interband transitions (see Fig. 2 in their paper), thus an extended Drude analysis is used to extract the optical quasiparticle self-energy ($\Sigma^{\sigma_1}(\omega)$, $\Sigma^{\sigma_2}(\omega)$) from the real and imaginary parts of the optical conductivity. Then the scattering rate $1/\tau(\omega)$ and mass enhancement factor $m'/(m_b)$ can be obtained from the optical quasiparticle self-energy by

$$-2\Sigma_{2\omega}^{\sigma_2}(\omega) = \frac{1}{\tau(\omega)} = \frac{\omega^2}{4\pi} \left( \frac{\sigma_1(\omega)}{\sigma_1^2(\omega) + \sigma_2^2(\omega)} \right)$$ (4)

$$1 - \frac{1}{\omega} \sum_{\omega}^{\sigma_1}(\omega) = \frac{m'}{m_b} = \frac{\omega^2}{4\pi} \left( \frac{\sigma_2(\omega)}{\sigma_1^2(\omega) + \sigma_2^2(\omega)} \right)$$ (5)
As the Fe-based superconductors are multi-band systems, here the self-energy should be regarded as an average of the contributions from the relevant bands.

As shown in Fig. [15], the scattering rate \( 1/\tau(\omega) \) continuously increases with frequency up to 1500 cm\(^{-1}\) with no saturation. A small kink with weak temperature dependence could be found around 500 cm\(^{-1}\). This kink in \( 1/\tau(\omega) \) corresponds to the 500 cm\(^{-1}\) peak in the real part of the self-energy (Fig. 15). Qazilbash et al. attribute this low energy feature to an electron-boson coupling mode as found in the high-T\(_c\) cuprates.\[84, 85\] Figure [15] also plots the \( \omega\tau=1 \) line and the scattering rate \( 1/\tau(\omega) \) at 10 K lies below this reference line, indicating well-defined quasiparticle excitations exist in LaFePO. The overall behavior of \( 1/\tau(\omega) \) is different from the optimally doped cuprates, in which a linear frequency dependence is found.\[84\] From the inset of Fig. [15], the mass enhancement factor \( (\omega \rightarrow 0) \) at \( T=10 \) K is \( 1.5\pm0.1 \), in good agreement with the renormalization factor of 2 obtained from ARPES and de Haas-van Alphen measurements.\[83, 86\] Considering the rather modest mass enhancement factor and its weak \( T \)-dependence, Qazilbash et al. conclude LaFePO is a moderately correlated metal.

4.2. \( Ba_{0.55}K_{0.45}Fe_2As_2 \)

Yang et al. investigate the normal state properties for \( Ba_{0.55}K_{0.45}Fe_2As_2 \) single crystal and also find evidence for bosonic mode coupling.\[70\] Since it is difficult to separate the Drude component and the interband transitions in K-doped \( BaFe_2As_2 \), several fits are used to extract the intra-band contribution for the extended Drude analysis. A bosonic excitation spectrum based on the spin fluctuation model was used to fit the scattering rate \( 1/\tau(\omega) \). The author find the coupling constant strongly dependent on temperature \( (\lambda=0.6 \) when \( T=295 \) K, \( \lambda=2.0 \) for \( T=28 \) K), suggesting that magnetic excitations are responsible for the scattering. A recent ARPES study in optimally doped \( Ba_{0.55}K_{0.45}Fe_2As_2 \) have found an unconventional mode with an orbital selective nature: a 25 meV mode exists strongly dependent on temperature \( (\lambda=\pm0.1) \) at \( T \) and vanishes above \( T_c \) for both the \( \alpha \) and \( \gamma \) bands, showing a strong temperature dependence and vanishes above \( T_c \), while no kink is found for the \( \beta \) band.\[87\] As the \( \alpha \) and \( \gamma \) Fermi surfaces are well connected by the SDW vector in the parent compound, Richard et al. therefore speculate the kink may originate from the enhanced antiferromagnetic fluctuations below \( T_c \).

5. Phonon

5.1. ReFeAsO system

The 1111-phase belongs to space group P4\( _{1} \)mm and point group D\(_{4h}\). The rare-earth ions, Fe, As and O(F) occupy 2c, 2b, 2c and 2a positions, respectively. Formal group analysis gives eight Raman active modes including two A\(_{1g}\), two B\(_{1g}\) and four E\(_{g}\) modes, and six infrared active modes including three A\(_{2g}\) and three E\(_{u}\) modes. Representatively eight Raman active modes of LaFeAsO are shown in Fig. [16] [88]. The first polarized Raman phonon measurements on La(Fe,Tm)AsO\(_{2}\) crystals were made by Hadjiev et al. under a microscope on very small plate-like single crystals obtained within polycrystalline samples.\[89\]

The four Raman modes with vibration out of FeAs plane were identified clearly, as shown in Fig. [17]. Zhao et al. reported Raman spectra obtained in doped and undoped LaFeAsO(F) and CeFeAsO(F) polycrystalline samples.\[88\] Zhang et al. studied the doping and temperature dependence of Raman spectra in NdFeAsO\(_{1-x}\)F\(_x\) polycrystalline samples.\[90\] Polarized Raman spectra on NdFeAsO\(_{1-x}\)F\(_x\) single crystals were presented by Gallais et al.\[91\] Interestingly, a strong resonant enhancement for the Fe-related phonon modes was found below 2 eV, which was considered to be related to the interband transition at 2 eV as observed in optical conductivity. Among all the Raman-active phonon modes, the B\(_{1g}\) mode of iron around 210 cm\(^{-1}\) is much more important in exploring the superconducting and SDW mechanism for Fe-based compounds. However, this mode is slightly sample-dependent from the above Raman measurements.

5.2. AFe\(_2\)As\(_2\) system

The 122-phase belongs to space group I4/mmm and point group D\(_{4h}\). Alkaline-earth ions, Fe and As occupy 2a, 4d and 4e positions, respectively. There are four Raman active modes including A\(_{1g}\), B\(_{1g}\) and two E\(_{g}\) modes, and four infrared modes including two A\(_{2u}\) and two E\(_{u}\) modes. Litvinchuk et al. carried out the Raman measurements on Sr\(_{1-x}\)K\(_{x}\)Fe\(_2\)As\(_2\) crystals (shown in Fig. [18]) and Choi et al. reported Raman results on CaFe\(_2\)As\(_2\) crystals.\[92\] Compared to the 1111 phase, B\(_{1g}\) phonon frequency in the 122-phase is almost the same as that in the 1111-phase, reflecting the fact that the vibration of Fe is dominated by Fe-As bonds.

5.3. Fe(SeTe) system

Fe(SeTe) is a prototype of Fe-based superconductors, which has the simplest formula without any separation layer. Its space group is P4\( _{1} \)mm and point group D\(_{4h}\). Fe and Se(Te) occupy 2a and 2c positions, respectively. It has four Raman modes including A\(_{1g}\), B\(_{1g}\) and two E\(_{g}\), and two infrared modes: A\(_{2u}\)
and $E_u$. As shown in Fig. 19, $A_{1g}$ mode of Te locates at 159 cm$^{-1}$. $B_{1g}$ mode of Fe is 196 cm$^{-1}$, slightly lower than that of FeAs-based compounds. However, a direct isotope experiment made by Liu et al.\[95\] indicated that the isotope effect of iron on superconducting and SDW transitions is quite large. The isotope effect is $\sim 0.4$, close to conventional BCS value. While the isotope effect of oxygen on $T_c$ is negligibly small. Apparently, further experiments are required to understand the issue. Recent X-Ray inelastic scattering experiment may present some hints on this question. It is suggested that a unconventional electron-phonon coupling may exist at certain wave vectors.\[96, 97, 98\]

5.5. Phonon behavior at the SDW/SC transitions

The SDW transition in the parent compounds is usually accompanied by a structural change. One may expect that phonon anomalies can be observed around the SDW transition temperatures. In principle the doubly-degenerated $E_g$ modes of Fe will be split to $B_{2g}$ and $B_{3g}$ modes after the transition from tetragonal to orthorhombic structures. There is no such splitting reported yet. The estimated splitting could be too small to be determined. However Raman measurements on SrFe$_2$As$_2$ crystals do not show such anomalies for the in-plane modes.\[92\] On the other hand, Raman measurements on CaFe$_2$As$_2$ crystals indicate that a large jump of $\sim 4$ cm$^{-1}$ of Fe $B_{1g}$ phonon occurs around the structural transition temperature 173 K.\[93\] The jump can not be explained by lattice distortion. It is suggested that the jump could be related to the change of electronic density at Fermi surface modified by structural transitions. For superconducting Sr$_{1-x}$K$_x$Fe$_2$As$_2$ and NdFeAsO$_{1-x}$F$_x$ crystals, no phonon anomalies can be seen cross $T_c$.\[81, 92\]

As shown in Fig. 2, five pronounced phonon modes at 100, 247, 265, 336, 438 cm$^{-1}$ dominate the far-infrared reflectivity $R(\omega)$ for polycrystalline LaFeAsO.\[5\] According to calculated PDOS (phonon density of states), the phonon modes above 300 cm$^{-1}$ are strongly oxygen-derived, while the phonons below 300 cm$^{-1}$ are a mixture of La, Fe, and As vibration.
have been devoted to finding out how and why superconductivity emergences from Fe 3d electrons. In retrospect, the most convinced and important spectroscopic results were obtained from 1111-type polycrystals and 122-type single crystals for the in-plane optical response. From the SDW gap in the metallic parent compounds, and the superconducting gap for the doped systems, we know the Fe-based superconductors (especially the 122 system) are different from the high-T, cuprates but more or less closer to the standard BCS superconductors. However, information on the charge dynamics for the c-axis, or the symmetry of the superconducting gap in single crystalline 1111-type Fe-based superconductor is still lacking. Moreover, investigations on the electronic correlation and the pseudogap-like feature in Fe-based compounds requires further studies, especially spectroscopic investigations on high-quality single crystals. Anyhow, some basic conclusions on Fe-based superconductors and their parent compounds can be made based on current optical and Raman data, which are briefly summarized as below.

*Itinerant system.* Almost all Fe-based superconducting systems are metallic in nature. In particular, the parent compound is not an antiferromagnetic Mott insulator, but a semimetal with an SDW instability. The plasma frequency in the normal phase (above $T_{SDW}$) is about 1.5 eV. When the nesting condition is weakened by either carrier doping or application of pressure, superconductivity wins in the ground state.

*Multi-band effect.* Fe-based superconductors are multi-band systems, which are different from the situation in cuprates (one-band). The BCS double-gap is observed in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ from ARPES measurement. With a detailed analysis of the optical conductivity, similar two-gap superconductivity can also be found in optical response. Another optical evidence for the multi-band property in iron arsenide is the SDW double-gap in AFe$_2$As$_2$ (Sr, Ba) parent compounds.

*s-wave superconductivity.* From optical measurement on polycrystalline ReFeAsO$_{1−x}$F$_x$, signature of the superconducting gap is observed at the far-infrared as an up-turn in reflectivity below $T_c$. More convinced evidence of the gap symmetry comes from optical data on single crystal. For optimally doped (Ba,K)Fe$_2$As$_2$, an s-wave pairing lineshape is found for the superconducting gap, thus different from the d-wave gap in cuprates.

*Electron-phonon coupling.* The large isotope effect implies that electron-phonon coupling may be strong in the system. However, considering its high $T_c$, it is unlikely that electron-phonon coupling dominates the pairing as that in conventional BCS superconductors. This issue needs further experimental and theoretical efforts in the future.

7. Acknowledgement

This work is supported by the National Science Foundation of China, the Knowledge Innovation Project of the Chinese Academy of Sciences, and the 973 project of the Ministry of Science and Technology of China.
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