1. Introduction

High temperature superconductors continue to attract attention due to their potential in fundamental research and applications. Major research involves finding superconductors with high transition temperature \( T_c \), suitable for making wires, high critical magnetic field, etc necessary for industrial applications. One of the most intriguing aspects of high temperature superconductivity is the observation of a pseudogap above \( T_c \) \([1–3]\). In the pseudogap phase, the spectral density of states (SDOS) exhibits an energy gap at the Fermi level at some \( k \)-points around the antinode in the Brillouin zone above \( T_c \), which persists up to another temperature scale, \( T^* \) \([4]\). The Fermi surface gradually grows with the increase in temperature around the nodal point as an arc called the ‘Fermi arc’ and the full Fermi surface appears at \( T^* \). The existence of this phase is considered to be one of the major features distinguishing unconventional superconductors from conventional ones.

Two schools of thought exist on the origin of the pseudogap phase in unconventional superconductors. One scenario proposes that the pseudogap represents paired electronic states without superconducting coherence \([5–8]\). In this picture, the superconducting transition temperature, \( T_c \), is the temperature where phase coherence amongst the wave functions of the electron pairs sets in, giving rise to resistance free electrical behaviour. The incoherent paired electronic states above \( T_c \) are the precursor to superconductivity. In the second scenario, the pseudogap is disconnected from superconductivity and is believed to arise due to other competing interactions such as a hidden order, spin fluctuations, etc \([9–11]\). These competing interactions are believed to culminate into a quantum critical point deep within the superconducting dome in the phase diagram.

The conventional superconductors are expected not to possess such complexity. Some recent studies, however, show signatures of a pseudogap even in conventional superconductors \([12–17]\). In most of these studies, however, the appearance of...
a pseudogap was often attributed to crystallographic disorder and/or reduced dimensionality as commonly observed in non-superconducting disordered metals [18–23]. Thus, the connection of the pseudogap (presumably arising due to extraneous effects) and its influence, if any, to superconductivity in conventional superconductors remains obscured. It is therefore desirable to search for a superconductor in which the spectral function at the Fermi energy reflects an intrinsic electronic structure free from dimensionality factors and/or disordered lattice potential. In this work, we choose a three-dimensional bulk compound, MgB2, which is a high temperature conventional superconductor and not nominally disordered. We present our high resolution photoemission spectroscopic results on specially prepared highly compact MgB2 [24, 25] as a function of temperature, which reveals the signature of a pseudogap in MgB2. The relatively high Tc (39 K; ΔTc = 0.2 K) of MgB2 presents a large temperature range to study the pseudogap physics in detail using traditional photoemission spectrometers equipped with a liquid helium cryomonomitor, which has a distinct advantage over other conventional systems. This material has been studied extensively in the literature using high resolution and angle resolved photoemission spectroscopy, and signatures of multiple gaps have been discovered [26–31]. Recently, Mou et al [31] employed laser based angle resolved photoemission to study the electronic structure with a very high energy resolution and found the signature of a σ gap (∼7 meV) and π gap (∼3 meV). Most of these high resolution studies focused in the energy range close to the Fermi level to probe the superconducting gap and its dependence on temperature. Here, we have focused on a somewhat larger energy scale and discovered interesting spectral evolution with temperature.

2. Experimental details

High resolution photoemission spectroscopic measurements were performed on highly compacted samples to minimize the extraneous effects due to impurities, grain-boundary oxides (particularly MgO) and extra phases, disorder, defects etc. The novel synthesis method patented by our group (apt to prepare bulks) is a concomitant grain growth method via direct synthesis from pure B (99.96%) and Mg (99.99%) put into outgassed Ta crucibles, sealed by arc welding in pure argon and subsequently, an annealing at 950 °C for 3 d was followed [32]. The final products are brown-blackish and extremely fine crystalline form. The samples possess a density value of the order of 2.3 g cm⁻³ with respect to a theoretical value of 2.6 g cm⁻³ calculated on the basis of the unit-cell volume. Magnetic and transport measurements exhibit that the pristine properties are optimal, Tc = 39.2 K and the superconducting transition is very sharp (ΔTc = 0.2 K). The quality of the MgB2 phase was studied by x-ray powder diffraction and scanning electron microscope—energy dispersive analysis of x-rays measurements. No free Mg or spurious phases were detected.

For photoemission spectroscopic measurements, the samples were fractured/scraped in situ (pressure <2 × 10⁻¹¹ Torr) at each temperature and cleanliness was confirmed by the absence of impurity features in both x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) measurements. Reproducibility of the spectra was ascertained after each cycle of surface preparation. Photoemission measurements were carried out using a monochromatic Al Kα x-ray source (hv = 1486.6 eV) for XPS and He Iα photon source (hv = 21.2 eV) for UPS employing a spectrometer equipped with SES2002 gammadata scienta analyzer with an energy resolution set to 300 meV for XPS and 1.4 meV for UPS measurements. XPS was used to monitor the growth of impurities on the sample surface. The temperature variation was achieved using an open cycle He cryostat from Advanced Research Systems, USA. The lowest temperature of 5 K could be achieved by pumping helium at the exhaust.

3. Results

In figure 1(a), we show the high resolution He Iα spectra collected at different temperatures across Tc. The signature of a distinct coherent peak close to the Fermi level, εF, followed by a dip at around 10 meV shown by an arrow is observed in the 5 K spectrum. Below Tc, the spectral weight at εF gradually
shifts towards higher binding energies, resulting in the opening up of an energy gap. This is demonstrated in figure 1(b); the spectral intensity at $\epsilon_F$ gradually reduces with the reduction in temperature. The thick solid line is the spectrum from Ag at 5 K. The lowest temperature case is shown in figure 1(c), where we show the high resolution 5 K He I $\alpha$ spectrum close to $\epsilon_F$ superimposed over the Ag spectrum collected from a scraped polycrystalline Ag sample under identical experimental conditions. The difference between the two spectra is clearly manifested in the figure. The leading edge of the MgB$_2$ spectrum appears at higher binding energy relative to the Ag spectrum implying the formation of the superconducting gap. In order to elucidate the spectral weight changes more clearly, we show the difference between the spectral intensity of MgB$_2$ and Ag by open triangles. There are three features in the difference spectrum as denoted by A, B and C—the existence of feature C is more comprehensible in an expanded intensity scale shown in the inset of (a). A division of the MgB$_2$ spectrum by the Ag spectrum that takes care of the Fermi–Dirac distribution induced spectral suppression across $\epsilon_F$ reveals more distinctly the signatures of A, B and C—both A & C are peaks, and B is a valley/dip representing the superconducting gap—a peak-dip-peak structure typical for a superconductor in the superconducting phase. The temperature evolution of the difference spectra shown in figure 1(d), demonstrates the gradual filling up of the dip and smearing of the peaks A & C with increasing temperature. Above $T_c$, all these features are smeared out. These spectral changes demonstrate the vanishing of the superconducting gap above $T_c$ commensurate to the predictions of the Bardeen–Cooper–Schrieffer (BCS) theory [13, 33–35].

The Fermi function broadening superimposed on the spectral functions renormalizes the changes expected from the many-body physics of the system. Thus, we extracted the SDOS by symmetrizing the experimental spectra, which often provides a good representation of SDOS, and has been found to be very helpful in analyzing the superconducting gap/pseudogap in cuprate superconductors as well as in other systems [4, 23, 36]. The effect of resolution broadening would be minimal due to high energy resolution of 1.4 meV employed in the experimental technique.

Since the symmetrization method implicitly assumes an electron-hole symmetry in the spectral function, the procedure of extraction of SDOS has been verified in figure 2(a) by comparing the SDOS obtained by symmetrization (line) and via division by the resolution broadened Fermi–Dirac function (symbols). Both look identical and this establishes the symmetric nature of the spectral function with respect to $\epsilon_F$. (b) Symmetrized spectral function of MgB$_2$ valence band spectra at different temperatures. (c) Spectral DOS obtained by the division of resolution broadened Fermi–Dirac function. (d) Symmetrized spectral DOS above $T_c$.

![Figure 2](image-url)

Figure 2. (a) Comparison of the spectral density of states at 200 K obtained by symmetrization (line) and via division by the resolution broadened Fermi–Dirac function (symbols). Both look identical and this establishes the symmetric nature of the spectral function with respect to $\epsilon_F$. (b) Symmetrized spectral function of MgB$_2$ valence band spectra at different temperatures. (c) Spectral DOS obtained by the division of resolution broadened Fermi–Dirac function. (d) Symmetrized spectral DOS above $T_c$. The Fermi function broadening superimposed on the spectral functions renormalizes the changes expected from the many-body physics of the system. Thus, we extracted the SDOS by symmetrizing the experimental spectra, which often provides a good representation of SDOS, and has been found to be very helpful in analyzing the superconducting gap/pseudogap in cuprate superconductors as well as in other systems [4, 23, 36]. The effect of resolution broadening would be minimal due to high energy resolution of 1.4 meV employed in the experimental technique. Since the symmetrization method implicitly assumes an electron-hole symmetry in the spectral function, the procedure of extraction of SDOS has been verified in figure 2(a) by comparing the SDOS obtained by symmetrization (line) and via division by the resolution broadened Fermi–Dirac function (symbols). Both look identical and this establishes the symmetric nature of the spectral function with respect to $\epsilon_F$. The latter procedure does not suffer from such effects and helps to extract the SDOS from high resolution data quite reliably. The figure shows an identical representation of SDOS obtained from both the procedures providing confidence on the analysis process adopted here. Thus obtained SDOS are shown in figure 2(b) exhibiting additional distinct signatures of a peak-dip-peak structure at low temperatures that gradually smears out with the increase in temperature. Here, the dip refers to the valley observed at 10 meV between the coherent feature and the spectral intensities at higher binding energies as shown by an arrow in figures 1(a) and 2(b).

Interestingly, the curves representing spectral intensities at different temperatures start to deviate from each other at around 50 meV binding energy (see figures 2(c) and (d)). Such spectral evolution with decreasing temperature is reminiscent
of a pseudogap formation in metals. We observe that SDOS at $\epsilon_F$ decreases monotonically with decreasing temperature in the normal phase ($T > T_c$) as shown separately in figure 2(d) for clarity. The peak-dip-peak structure below $T_c$ corresponding to the superconducting gap appears to emerge from the pseudogap at $T > T_c$. In order to explore the evolution of this pseudogap with temperature, we simulated the spectral function assuming a phenomenological self energy of the form, $\Sigma_\alpha(\epsilon) = -i\Gamma_1 + \Delta_p^2/[(\epsilon + i\Gamma_p) + \epsilon_k]$, where the second term represents the effect due to electron–phonon coupling. $\Gamma_1$ is the single particle scattering rate. $\Delta_p$ and $\Gamma_p$ represent the pseudogap and lifetime of the phonon-dressed electrons in the system. The electron–phonon coupling constant, $\lambda$, can be expressed as $\lambda = D_{\text{sp}} \langle \bar{I}^2 \rangle / M < \omega^2 >$, where $D_{\text{sp}}$ is the density of states (DOS) at $\epsilon_F$ per spin per atom, $< \bar{I}^2 >$ is the square of the averaged electron-ion matrix element involving lattice vibrations, $M$ is the atomic mass, and $< \omega^2 >$ is the average of the square of the phonon frequencies [37]. The product $M < \omega^2 >$ does not depend on the mass, but on the force constants, while $\eta = D_{\text{sp}} < \bar{I}^2 >$, known as the Hopfield factor, is purely an electronic property and depends on the spectral function at $\epsilon_F$. $\Delta_p$ provides a measure of the pseudogap due to the renormalized spectral function at $\epsilon_F$ and both $\Gamma_p$ & $\Delta_p$ depend on $\lambda$.

The simulated SDOS shown by the solid line in figure 3(a) provides an excellent representation of the experimental SDOS. A small deviation at $\epsilon_F$ appears at $35 K$, which is below $T_C$ due to the emergence of the superconducting gap. The corresponding parameters are shown in figures 3(b) and 3(c). The single particle scattering rate is found in the range of $0.1–0.2 eV$ as expected. The value of $\Gamma_p$ is about $65–70$ meV indicating the finite lifetime of the electron–phonon coupled states. The pseudogap of about $65–70$ meV found here matches remarkably well with the energy of the $E_{2g}$ phonon mode found in Raman studies, which is believed to be responsible for the BCS-type superconductivity in this system [38, 39]. Small increases in $\Delta_p$ and $\Gamma_p$ with the decrease in temperature may be attributed to the increase in spring constant at lower temperatures.

In order to verify the influence of disorder in the spectral function, we plot SDOS as a function $(\epsilon - \epsilon_F)^\alpha$ with different numerical values of $\alpha$ in figure 4. In the case of disordered metals, it is well known that the SDOS varies as $(\epsilon - \epsilon_F)^{0.5}$ [18–20]. We chose to study the SDOS at temperatures above $T_c$ in order to exclude the influence of the BCS spectral function over the SDOS. In figure 4(a), $\alpha = 2$ gives rise to non-linear behaviour with a downward curvature and $\alpha = 0.5$ results in an upward curvature (see figure 4(b)). Evidently, the optimal $\alpha$ value lies between 0.5 and 2 indicating a deviation from the simple Fermi liquid behaviour as found in other systems [17, 23, 40, 41]. Interestingly, for $\alpha = 1.5$, a linear behaviour of SDOS is observed (see figure 4(c)), which has often been attributed to the influence of the coupling of electron to collective excitations such as magnon in magnetic materials [40, 42, 43]. The observation of a 1.5 exponent in non-magnetic MgB$_2$ indicates a link of the spectral functions and collective excitations.

The spectral function close to $\epsilon_F$ is simulated using a phenomenological self energy as a function of superconducting gap ($\Delta$), electron pair lifetime ($\Gamma_0$) and single particle scattering rate ($\Gamma_1$) following the procedure used earlier [4, 17] and superimposed over the symmetrized spectra in figure 4(d). Since the spectral change due to the superconductivity occurs at an energy scale of about 5 meV (quasiparticle binding energy) in MgB$_2$, we use an energy range of about $\pm 10$ meV across $\epsilon_F$ of the experimental spectra for fitting. Figure 4(d) shows the results of the simulations with remarkably good representation of the experimental spectra for a realistic sets of parameters shown in figure 4(e) [4, 26]. The temperature evolution is captured by the variation of the parameters reasonably well. The single particle scattering rate, $\Gamma_1 = 0.2$ eV found in this energy range is similar to the value found at higher energy range at high temperatures. The superconducting gap, $\Delta$ gradually decreases with the increase in temperature and

**Figure 3.** (a) Fit of the spectral density of states at different temperatures. Symbols are the experimental data and lines are the fit. (b) Pseudogap, $\Delta_p$, and the lifetime, $\Gamma_p$, of the phonon coupled charge carriers are shown as a function of temperature. (c) Single particle scattering rate, $\Gamma_1$, as a function of temperature.
vanishes at and above $T_c$. The temperature dependence [27] can be represented by $\Delta(T) = \Delta(0) \sqrt{1 - (T/T_c)^\beta}$ with $\beta = 3.0$ and $T_c = 39.2$ K. This indicates a typical BCS-type superconductivity in this material with $\Delta(0) = 4$ meV and $T_c = 39.2$ K consistent with the transport data [26–30].

4. Discussion

The above experimental results (specifically, the analysis in figure 4) establish that the superconducting gap in MgB$_2$ vanishes at the superconducting transition temperature as expected in a typical BCS-type superconductor. However, figures 2 and 1 reveal a distinct pseudogap surviving at temperatures much higher than its $T_c$, which is unusual for a BCS superconductor. The absence of the reference of this feature in earlier high resolution studies presumably due to the fact that in most of those studies, the energy range probed is much smaller than that required for this feature. It is difficult to associate the pseudogap in this compound to the survival of Cooper pairs above $T_C$ as observed in cuprate superconductors since the energy scales are very different in MgB$_2$ while in cuprates, the pseudogap above $T_C$ scales well with the superconducting gap leading to the claim that Cooper pairs exist above $T_C$. Absence of $(\epsilon - \epsilon_F)^{0.5}$ dependence of the SDOS seen in figure 4 implies that the role of crystalline disorder can also be ruled out as the cause of the pseudogap.

The binding energy at which SDOS starts to decrease with temperature and the size of the pseudogap corroborate well with the $E_{2g}$ phonon excitations involving vibration of B-atoms in the B-sublattice [38, 39], which is believed to cause superconductivity in this material. Thus, the pseudogap can be attributed to the electrons coupling to collective excitations of the crystal lattice (phonons) as also found in various other systems [12–14, 17]. These results bring out an important question of the association of a pseudogap to the electron–phonon coupling as a generic behavior of BCS superconductors. On the experimental front, the major difficulty in such studies is the low $T_C$ of most of the BCS superconductors, which is not easily accessible by photoemission.
studies. While it is hoped that technological advancement would make these low temperatures accessible for photoemission studies in the future, the signature of electron–phonon coupling induced superconductivity is manifested as an isotope effect in BCS superconductors. Interestingly, the \( T_c \) is often found to be smaller for heavier isotopes [24], which is in line with the attribution of electron–phonon coupling induced depletion of spectral intensity at the Fermi level.

Some experiments on cuprates also exhibit a high energy pseudogap (\( \sim 0.1 \) eV in addition to the ones associated with the Fermi arcs) scaling with the characteristic temperature/energy scales arising due to the antiferromagnetic correlations or short range antiferromagnetic order in the system [44–46]. It is to be noted that the presence of electron phonon interaction is theoretically explained in the normal state of MgB\(_2\) [47]. Furthermore, the continuous temperature evolution (without any anomaly) of the frequency across \( T_c \) and linewidth of the Raman spectra from the \( E_{2g} \) phonon mode lend further credence to our finding of the electron phonon coupling induced effect in the spectral function above \( T_c \) [48].

An important contrast with the cuprate superconductors is that there are two kinds of pseudogap present in cuprates—(i) the high energy one (\( \sim 0.1 \) eV) is associated to the antiferromagnetic order and (ii) the ones forming Fermi arcs appear to merge with the superconducting gap i.e. energy scale of the second case is similar to the energy scale of the superconducting gap. In MgB\(_2\), the energy scale over which the pseudogap is observed is much larger (\( \geq 50 \) meV) than the energy scale over which superconducting gap is observed (\( \sim 4–6 \) meV) and is similar to the first case in cuprates. Our observation makes an impression that the superconducting gap emerges within the pseudogap formed due to electron phonon coupled objects. The pseudogap consisting of electrons coupled to phonons with a finite lifetime presumably provides the necessary platform for electrons within a certain energy range to form Cooper pairs and cause superconductivity.

5. Conclusions

In summary, we have studied the electronic structure of MgB\(_2\) employing high resolution photoemission spectroscopy. The experimental valence band photoemission results show the presence of a pseudogap in MgB\(_2\) in the normal phase and a superconducting gap below \( T_c \). The energy scale over which the pseudogap forms (\( \sim 65–70 \) meV) is significantly larger than the energy scale of the superconducting gap (\( \sim 4–6 \) meV) and corroborates well with the \( E_{2g} \) phonon excitations of the system. A probable picture of superconductivity in MgB\(_2\) can be conjectured to be the one where the electron pairs causing superconductivity emerge from the electron–phonon coupled species already formed above \( T_c \).

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