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Isotope Effect on Electron-Phonon Interaction in Multiband Superconductor MgB₂

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We investigate the effect of isotope substitution on the electron-phonon interaction in the multiband superconductor MgB₂ using tunable laser based Angle Resolved Photoemission Spectroscopy. The kink structure around 70 meV in the σ band, which is caused by electron coupling to the E_{2g} phonon mode, is shifted to higher binding energy by ~ 3.5 meV in Mg¹⁰B₂ and the shift is not affected by superconducting transition. These results serve as the benchmark for investigations of isotope effects in known, unconventional superconductors and newly discovered superconductors where the origin of pairing is unknown.

I. INTRODUCTION

The discovery of the isotope effect in conventional superconductor played a key role in establishing Bardeen-Cooper-Schrieffer (BCS) theory¹⁻⁴, in which electrons form Cooper pairs by coupling via lattice vibrations (phonons). The isotope effect is regarded as a decisive method to determine whether or not the pairing in newly discovered superconductors is phonon mediated, or of unconventional (e. g. electron-electron) origin. This approach worked beautifully in case of the MgB₂ superconductor^{5,6} and immediately established electron-phonon coupling as the origin of pairing and superconductivity in this material⁶. The phonon mediated superconductivity in this material was explained by multiband BCS/Eliashberg theory shortly after its discovery⁶⁻⁹. Similar measurements have been made on cuprate high temperature superconductors, but no unambiguous conclusion has been reached because of the complexity of isotope response and inconsistent results¹⁰⁻¹³. Thus, MgB₂ is unique in its combination of very high T_c values and unambiguous electron-phonon coupling.

The electron-boson interaction renormalizes the binding energy of the electrons near chemical potential, causing a “kink” structure in the band dispersion which is a signature of a sudden change of self-energy due to coupling to the bosonic mode. Angle Resolved Photoemission Spectroscopy (ARPES), a powerful tool that can measure the band dispersion and self-energy with momentum resolution, provides a direct way to study the electron-boson interaction. The kink structure in cuprate high temperature superconductor has been intensively investigated by ARPES for years because it might contain essential information to establish the high temperature superconducting mechanism¹⁴. But whether the observed kink is related to phonon or spin fluctuation is still an open question. There were several ARPES-based studies of the isotope effect in cuprates superconductors carried out in the past¹⁵⁻¹⁸. The results included observation of a very large change in band dispersion at high binding energies, interpreted as a signature of polaronic effects¹⁵ and observation of very small effect at low energies along the nodal direction¹⁸. Due to difference in conclusions the significance and relation to high tempera-

ture superconductivity remains unclear. Surprisingly, to the best of our knowledge no direct experimental study of the isotope effect on the kink structure in a classical BCS superconductor has been reported. MgB₂ offers a unique opportunity due to its relatively high T_c and its quasi two dimensional character of the σ bands.

MgB₂ is a layered multiband superconductor with a transition temperature as high as 40 K^{5,6}. The strong electron-phonon interaction and discovery of large isotope effect on T_c ^{6,7} make this material an ideal system for the investigation of this important topic and establish benchmarks for gaining insights to novel superconductors. Early ARPES studies of MgB₂ did not reveal the kink structure because of experiment resolution and sample quality and size limitations¹⁹⁻²¹. Recently, the kink structure was identified using our tunable laser ARPES system with much improved instrumental resolution^{22,23}. This provides us the opportunity to study the isotope effect on the kink structure in a prototypical conventional superconductor. In this letter, we report an ARPES study of the electron-phonon interaction in Mg¹⁰B₂ and Mg¹¹B₂ samples. We will show the clear isotope shift of the kink structure on the σ band and that this isotope shift is not significantly affected by the superconducting transition.

II. EXPERIMENTAL DETAILS

MgB₂ single crystals are usually grown from a solution with excess Mg under high pressure and high temperature in BN crucibles²⁴. Unfortunately, for isotopic substitution, there are clear indications that BN is partly reacting with Mg during the high pressure/high temperature growth process. The incorporation of BN into the high temperature melt is suggested by the growth of BN single crystals together with MgB₂ and is clearly implicated by the fact that MgB₂ crystals grown with nominally, isotopically pure ¹¹B contain detectable and enhanced levels of ¹⁰B that appears to be coming from the BN crucibles made from natural abundance B²⁵. To avoid any contamination from natural B contained in the BN crucible, we performed the MgB₂ growths using MgO crucibles. Under these conditions, only single crystals of MgB₂ form

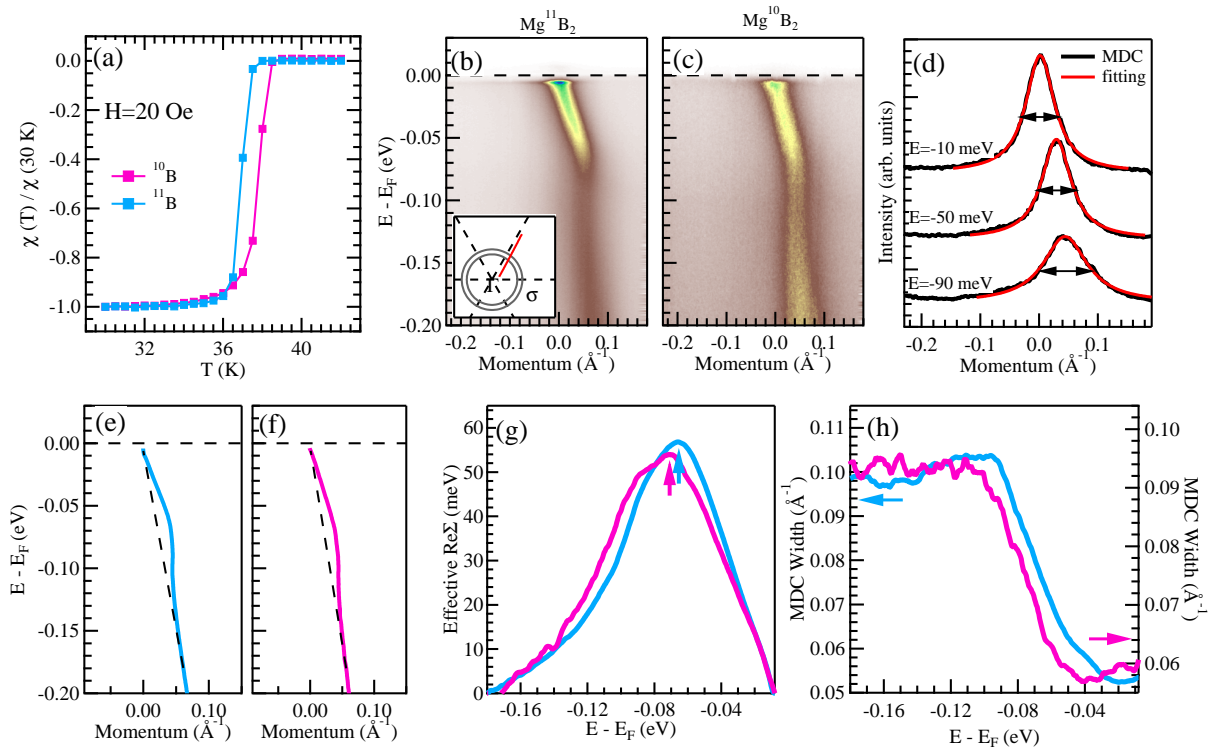


FIG. 1. (Color online) Isotope effect on kink structure in MgB₂. (a) Temperature dependence of magnetic susceptibility of Mg¹¹B₂ and Mg¹⁰B₂ single crystals used in ARPES measurements. (b)-(c) ARPES intensity plots for Mg¹¹B₂ and Mg¹⁰B₂ samples along a cut that crosses σ band measured at 15 K. (d) MDCs and Lorentzian fits at three sample binding energies. Horizontal arrows mark the MDC width that is proportional to $\text{Im}\Sigma$. (e) Band dispersion extracted by fitting the MDC data with Lorentzian function for Mg¹¹B₂ sample, as shown in panel (d). Dashed lines are corresponding bare bands used to extract the $\text{Re}\Sigma$. (f) same as (e), but for Mg¹⁰B₂ sample. (g) Effective $\text{Re}\Sigma$ obtained by subtracting the “bare” band dispersion (dashed lines in (e, f)) from extracted dispersion. Kink positions are marked with arrows. (h) Energy dependence of the MDC width.

and the isotopic purity of B can be preserved. The success of these growths also demonstrates that MgB₂ single crystals can be grown from a binary melt when adequate pressure is used to both control vapor pressure and shift the phase lines in the binary phase diagram. Single crystals of both Mg¹¹B₂ and Mg¹⁰B₂ were grown in the following manner using high purity Mg as well as 99.5% isotopically pure ¹¹B and ¹⁰B from Eagle Pitcher. Elemental Mg and B were placed in a thin walled MgO crucible in the ratio of Mg:B 1:0.7. Using a cubic anvil furnace, we apply around 3.5 GPa pressure on the sample at room temperature, then the temperature is increased to 1450 °C over approximately 2 hours, after dwelling at 1450 °C for 2 hours, the temperature is decreased to 650 °C over 6 hours. At this point the heater is turned off, quenching the growth to room temperature and pressure is decreased back to ambient. The MgO crucible is then removed from the pressure media and the excess Mg is distilled off of the MgB₂ crystals.

The typical size of the samples used in ARPES measurements was $\sim 0.3 \times 0.3 \times 0.2 \text{ mm}^3$. Samples were cleaved *in situ* at a base pressure of lower than 8×10^{-11} Torr. ARPES measurements were carried out using a

laboratory-based system consisting of a Scienta R8000 electron analyzer and tunable VUV laser light source²⁶. The energy resolution of the analyzer was set at 1 meV and angular resolution was 0.13° and $\sim 0.5^\circ$ along and perpendicular to the direction of the analyzer slits, respectively. All data were acquired using a photon energy of 6.7 eV; only the electronic structure of the two σ bands around Brillouin zone center can be measured with this photon energy. Fortunately it is the σ band that couples strongly with the phonons. The laser beam was focused to a spot with a diameter $\sim 30 \mu\text{m}$. Samples were cooled using a closed cycle He-refrigerator and the sample temperature was measured using a silicon-diode sensor mounted on the sample holder. The energy corresponding to the chemical potential was determined from the Fermi edge of a polycrystalline Au reference in electrical contact with the sample. In every temperature dependent measurement, aging effects were checked by thermal cycling. The consistency of the data was confirmed by measuring several samples.

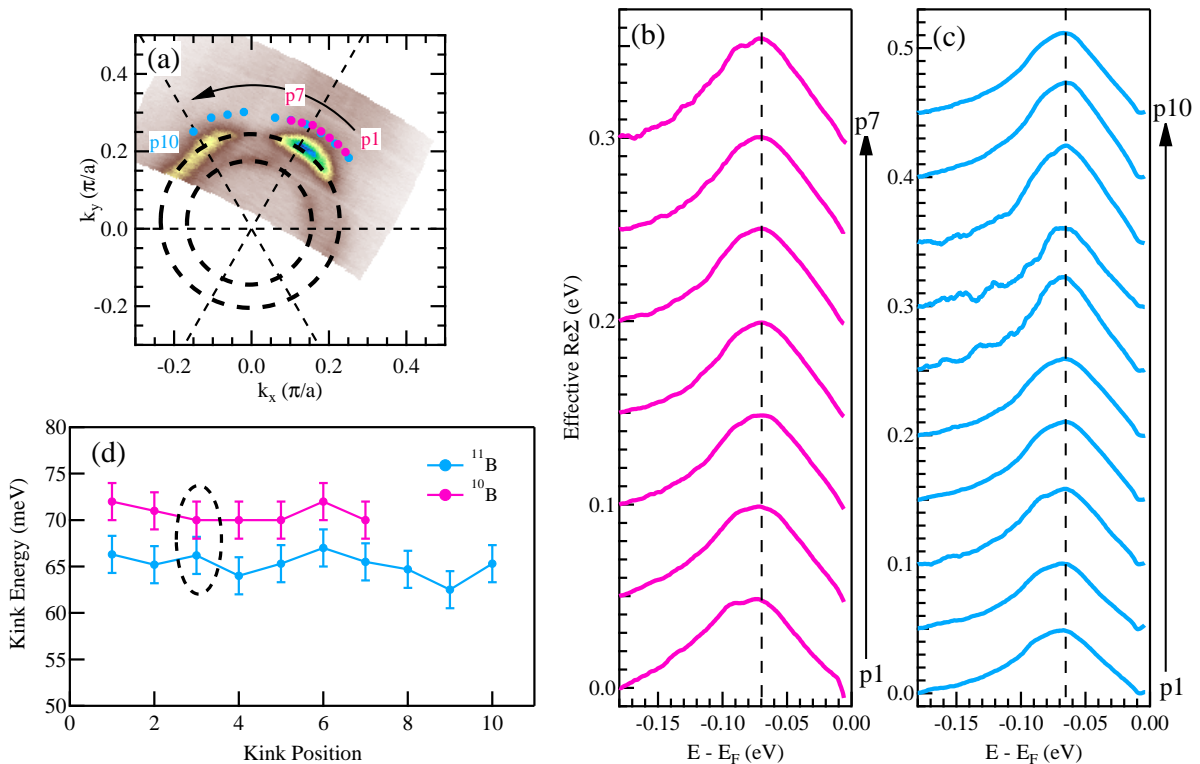


FIG. 2. (Color online) Momentum dependence of the kink structure. (a) Measured Fermi surface of Mg¹⁰B₂ at 40 K. (b)-(c) Momentum dependence of the effective $\text{Re}\Sigma$ of outer σ band in Mg¹⁰B₂ (b) and Mg¹¹B₂ (c). Data were taken at 20 K. (d) Momentum dependence of the kink energy obtained from (b) and (c). Corresponding kink structure positions in Brillouin Zone are mark with circles in (a). The data points in Fig. 1 are circled out.

III. RESULTS AND DISCUSSION

Fig. 1a shows the low field, temperature dependence of the magnetization for representative crystals of Mg¹⁰B₂ and Mg¹¹B₂. A clear, approximately 1.0 K isotope shift is seen in these data. It should be noted that each transition is lower by approximately 1.0 K ($T_c(^{11}\text{B})=37.5$ K, $T_c(^{10}\text{B})=38.5$ K) from what was previously reported in ref.⁶. This is due to the fact that the high pressure growth requires the use of a graphite heater in close proximity to the Mg-B melt. This leads to a small carbon substitution ($\sim 1\%$) that mildly suppresses T_c . The measured ARPES data in the superconducting state ($T=15$ K) of ¹¹B and ¹⁰B samples are shown in Fig. 1b and 1c. We chose a particular cut position in the momentum space (see the measured Fermi surface in Fig. 2a) where the matrix element totally suppresses the intensity of the inner σ band to simplify the data analysis. The anomaly in the band dispersion (kink) can be clearly seen directly in the the ARPES intensity plots around a binding energy of 70 meV and is caused by the coupling of the electrons to the E_{2g} phonon mode as discussed in our previous report²².

In order to quantitatively analyze the details of this kink structure, we extracted the band dispersion by fitting the Momentum Distribution Curves (MDC) with

Lorentzian lineshape as shown in Fig. 1d. The resulting band dispersion is shown in panels (e) and (f) for samples containing each of the boron isotopes. The effective real part of self-energy ($\text{Re}\Sigma$) is then obtained by subtracting a linear “bare” band dispersion (plotted as a dashed lines in panels e, f) from the measured dispersion and shown in Fig. 1g. Clearly visible peak is due to interaction of the electrons with phonon mode. The shape of this peak is slightly asymmetric, which is due to fact that $\text{Re}\Sigma$ is an antisymmetric function about E_F . The slight shoulder on the high binding energy side is most likely a reflection of complexity of electron-phonon interaction rather than a separate mode. The width of the MDCs is a measure of the imaginary part of the self energy ($\text{Im}\Sigma$) and is enhanced for the binding energies higher than the energy of the boson mode plus superconducting gap as plotted in Fig. 1h. Both the shape of $\text{Re}\Sigma$ (Fig. 1g) and MDC width (Fig. 1h) show a shift toward higher binding energy in ¹⁰B sample, providing clear evidence of the strong isotope effect in this material. Theoretically, either the peak position in $\text{Re}\Sigma$ or the midpoint of dropping edge in $\text{Im}\Sigma$ can be used to extract coupling boson mode energy, but the $\text{Re}\Sigma$ is more accurately extracted from data fits (it is easier to extract peak position than its width) and is more commonly used in literature¹⁴. The energy value of the $\text{Re}\Sigma$ peak is 66.5 meV for ¹¹B sample and 70

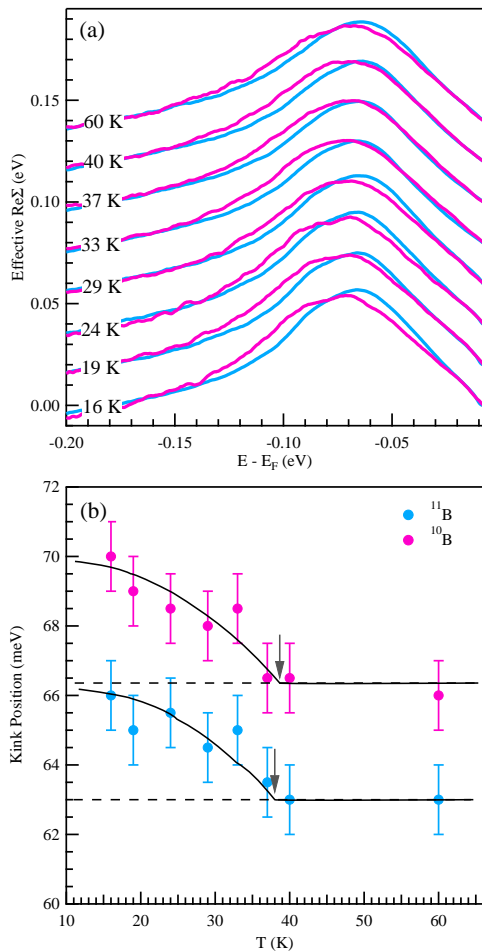


FIG. 3. Temperature dependence of the $\text{Re}\Sigma$ for the samples made using two different boron isotopes. (a) Effective $\text{Re}\Sigma$ for the outer σ band extracted from data measured at different temperatures. Cut position is the same as in Fig.1. (b) Temperature dependence of the kink energy for the two isotopes. Solid lines are guide for the eye. Arrows show corresponding transition temperatures from Fig. 1.

meV for ^{10}B sample respectively. Therefore the effects of different isotope mass on the energy of the phonon mode amounts to shift of ~ 3.5 meV

In order to confirm that the observed isotope energy shift does not arise due to some small angular misalignment associated with two measurement of two separate crystals, we measured the momentum dependence of the kink structure in both samples over a wide angular range. Following the same procedure as described above, we extracted the effective $\text{Re}\Sigma$ along different cuts in momentum space in Fig. 2b (^{10}B sample) and Fig. 2c (^{11}B sample) and the momentum dependent kink energy in Fig. 2d. The energy position of kink structure is nearly momentum independent in both samples demonstrating that the reported here shift of the kink energy attributed to the isotope effect is not due to an artificial caused by slight misalignment during measurement, which was a

likely culprit in early isotope experiments in cuprates¹⁵.

Finally we turn to the temperature dependence of the isotope effect. We compare the extracted $\text{Re}\Sigma$ of the outer σ band at different temperatures in Fig. 3a. The shift of the peak structure is obvious for all measured temperatures up to 60 K. In fig. 3b, we extracted temperature dependent peak position of $\text{Re}\Sigma$ in both samples. The temperature dependence of the kink position in ^{11}B samples was already discussed in our previous report²². The kink energy remains constant in the normal state and starts to shift to high binding energy gradually below T_c with a total shift of ~ 3 meV at the lowest measured temperature. The kink position in ^{10}B sample has a similar temperature dependence as that in ^{11}B sample and also shifts towards a higher binding energy by ~ 3.5 meV, indicating the isotope effect on kink structure is not affected by the superconducting transition in MgB_2 . The lifetime of the quasiparticles in the σ band is expected to be dominated by intraband scattering²⁷. If the kink position below T_c is at energy of $\Omega_{2g} + \Delta_\sigma$ ²⁸, the energy shift should be $\Delta_\sigma \sim 7$ meV. This number should be even larger once the hardening of E_{2g} mode reported by Raman measurements is taken into consideration²⁹. Further work is needed to understand why the kink energy shift below T_c is much reduced in MgB_2 .

The partial isotope coefficient α_M is defined as $\alpha_M = -\frac{d \ln T_c}{d \ln M}$, where M is atomic mass (see, for example, Ref.⁶). In standard BCS theory, α_M is equal to $1/2^4$, while the measured partial isotope coefficient of Boron in MgB_2 is substantially reduced to $0.26 \sim 0.31$ ^{6,7}. The deviation of α_B from standard $1/2$ was previously interpreted as an effect of Coulomb repulsion pseudopotential (μ^*) or strong phonon-phonon interaction (phonon anharmonicity)^{7,9,30}. Early theoretical³¹ and experimental³² results support the notion that large phonon anharmonicity exists in MgB_2 , but were subsequently shown to be incorrect by theory and experiment^{33,34} as well as later reports^{35,36}. In the harmonic limit, the phonon vibration frequency is directly proportional to the square root of atomic mass. We can use the kink energies measured by ARPES, which represent the energy of E_{2g} phonon in the two isotopic MgB_2 samples, to check the harmonicity of this mode. The ratio of the measured the kink energy ($\frac{\omega_{B11}}{\omega_{B10}} = \frac{63}{66} = 0.95 \pm 0.03$) is very similar to the inverse ratio of the square root of B atomic mass for the two isotopes ($\sqrt{\frac{M_{B10}}{M_{B11}}} = \sqrt{\frac{10}{11}} = 0.95$). These results suggest that the E_{2g} phonon in MgB_2 is likely in the harmonic limit. Most likely, the above discrepancy is resolved when two-phonon processes are taken into account³⁰.

In conclusion, we measured the isotope effect on the kink structure of MgB_2 superconductor. A shift of 3.5 meV is revealed between kink structure energy for B^{10} and B^{11} samples. Although the kink position shows a slight change below T_c in both samples, the isotope effect on kink structure is not affected by superconducting transition. Our results provide the first insights into the

effects of the isotope substitution on electron-phonon interaction in a prototypical, conventional superconductor and will serve as baseline for understanding phonon effects in yet to be discovered novel superconductors.

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