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Superconducting transitions studied by ultrahigh-resolution photoemission

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Abstract

Superconducting transitions of elemental metals and Ni borocarbides are studied using ultrahigh-resolution and low-temperature photoemission spectroscopy. Photoemission spectra of elemental metals (Nb and Pb) show the appearance of a sharp peak just below the Fermi level and a shift of the leading edge, indicating clear opening of the superconducting gap. Furthermore, Pb spectrum shows a dip and hump structure beyond the peak, characteristic of the strong-coupling superconductivity. On the other hand, comparative study of $Y(Ni_{1-x}Pt_x)_2B_2C$ ($x=0.0$ and 0.2) shows a difference in the slope of the leading edge, which can be explained in terms of a highly anisotropic s-wave gap in YNi_2B_2C, consistent to magnetic field dependent specific heat measurements. These observations demonstrate that photoemission spectroscopy is a useful and reliable technique to study electronic structures and phase transitions at very small energy scales. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ultrahigh-resolution and low-temperature photoemission spectroscopy; Superconducting transition; Strong-coupling superconductivity; Anisotropic s-wave gap

1. Introduction

The superconducting energy gap is a fundamental parameter determining superconducting properties [1]. The magnitude of the gap directly relates to the strength of the coupling between electrons and its momentum (k)-dependence sheds light on the origin of the pairing force. In 1960s, just after the Bardeen Cooper and Schriefer theory for superconductivity (BCS theory [1]), tunneling spectroscopy started revealing superconducting electronic structures of elemental superconductors, giving experimental support for the BCS theory and also indicating the need for the strong-coupling theory [2].

As for photoemission spectroscopy, energy resolution has been drastically improved in the late 1980s [3], mostly due to the motivation to measure the superconducting gap of the high temperature superconductors (high-T_c). Because of the advance in energy resolution, together with its capability of measuring k-resolved electronic structure, angle-resolved photoemission spectroscopy (ARPES) has established $d_{x^2-y^2}$-wave symmetry [4] and has also observed a pseudogap in the normal state with the same symmetry as the superconducting gap [5].

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These results have provided important experimental information to understand the mechanism of the superconductivity in the high-T_c cuprates. However, results for conventional superconductors showing a clear superconducting gap and the expected pile-up in the density of states (DOS) have been limited due to the energy resolution and sample cooling technique of spectrometers. The absence of reference spectra of conventional superconductors with low transition temperature (low-T_c) has even weakened the justification of photoemission results of the high-T_c superconductors. From an experimental point of view, limitation of photoemission spectroscopy for studying lower energy scales has been discussed [6]. Therefore, confirming whether the superconducting transition of low-T_c superconductors can be detected, or not, has been an important and challenging issue.

In this paper, we present photoemission results of low-T_c superconductors. For simple metals (Nb and Pb), we discuss the direct observation of the superconducting gap as well as fine structures induced by phonons. For Ni borocarbides, we show that the anisotropy of the superconducting gap can be studied due to the unprecedented energy resolution. These observations demonstrate that photoemission spectroscopy is a useful and reliable technique to study electronic structures (or phase transitions) having very small energy scales. In addition, we briefly explain the ultrahigh-resolution and low-temperature spectrometer constructed in order to study the superconducting transition of the low-T_c superconductors.

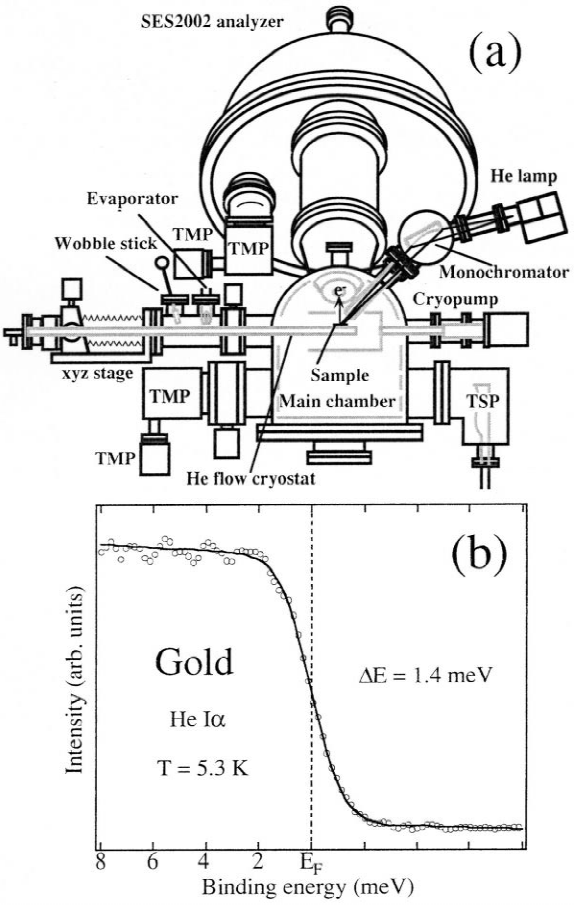

Fig. 1. (a) Schematic diagram of ultrahigh-resolution and low-temperature photoemission spectrometer and (b) ultrahigh-resolution photoemission spectrum of gold (open circles) together with a FD function of 5.3 K convolved by a Gaussian of FWHM of 1.4 meV (solid line).

2. Experimental

In Fig. 1a, we illustrate a schematic diagram of the spectrometer, which is equipped with a Scienta SES2002 electron analyzer, a GAMMADATA high-flux discharging lamp with a toroidal grating monochromator, and a flowing liquid He cryostat with a newly designed thermal shield which also works as a cryopump. The sample temperature is measured using a silicon-diode sensor mounted near the sample and the temperature can be controlled from 4 K (with pumping of He) to 300 K. The main chamber is pumped with two turbo molecular pumps (TMP) connected in series, and the base pressure is better than 5×10^{-11} Torr.

As determined from a gold Fermi edge spectrum (Fig. 1b), the highest energy resolution we achieve is 1.4 meV, including the energy width of the He Iα resonance line of 1.1–1.2 meV. This indicates that the resolution of the analyzer is nearly 0.8 meV and therefore we can obtain micro-electronvolt resolution using a higher resolution phonon source in the near future.

High-purity polycrystalline samples of Nb (T_c= 9.26 K) and Pb (T_c=7.19 K) were used in this study. Single crystals of $Y(Ni_{1-x}Pt_x)_2B_2C$ (T_c=15.4 K for x=0.0 and T_c=12.1 K for x=0.2) were grown by a floating zone method [7]. Magnetic susceptibility

measurements were carried out to confirm the superconducting T_c-values. Samples were scraped in-situ with a diamond file to obtain clean surfaces and spectra were obtained after ensuring thermal equilibration of samples. For the present study, we set the energy resolution at 2.0–2.3 meV in order to obtain a reasonable count rate. We did not see any spectral changes near the Fermi level (E_F) during our measurement time, indicating that the observed spectra are reflecting intrinsic electronic structures. Temperature-dependent spectral changes were confirmed by cycling temperature across T_c. E_F of samples was referenced to that of a gold film evaporated onto the sample substrate and its accuracy is estimated to be better than ± 0.05 meV.

3. Photoemission results of elemental metals: superconducting gap and phonon-induced fine structures

Fig. 2 shows the photoemission spectra of Nb measured at 5.3 and 12.0 K across the superconducting transition. The spectra of superconducting and normal states were normalized for area under the curve from 30 to -10 meV binding energy. While the 12.0 K spectrum shows a Fermi-edge structure, the spectrum at 5.3 K shows a sharp peak at 2.7 meV binding energy with a shift of the leading edge to higher binding energy and with redistribution of spectral weight up to 15 meV compared to the normal state spectrum. The observed change in the spectral shape represents opening of a superconducting gap. Similarly, Fig. 3 shows gap formation in the Pb spectrum, a sharp peak at 2.5 meV, followed by a fine structures (we discuss this later). We estimate values of the gaps using a Dynes function [8] fit (insets of Figs. 2 and 3) to the peak and the leading edge. We obtain values of $\Delta(5.3\ \mathrm{K})=1.35$ meV and a $\Gamma=0.10$ meV for Nb, and $\Delta(5.3\ \mathrm{K})=1.20$ meV and a $\Gamma=0.08$ meV for Pb. Using the measured values of $\Delta(5.3\ \mathrm{K})$ and the known dependence of the reduced energy gap $\Delta(T)/\Delta(0)$ versus reduced temperature (T/T_c) from strong-coupling theory [9] (which is also very similar to the BCS weak-coupling result as well as other experiments), we obtain values of $2\Delta(0)/k_BT_c$ for Nb to be 3.7 and for Pb to be 4.9. These values of $2\Delta(0)/k_BT_c$ are in good agreement with values

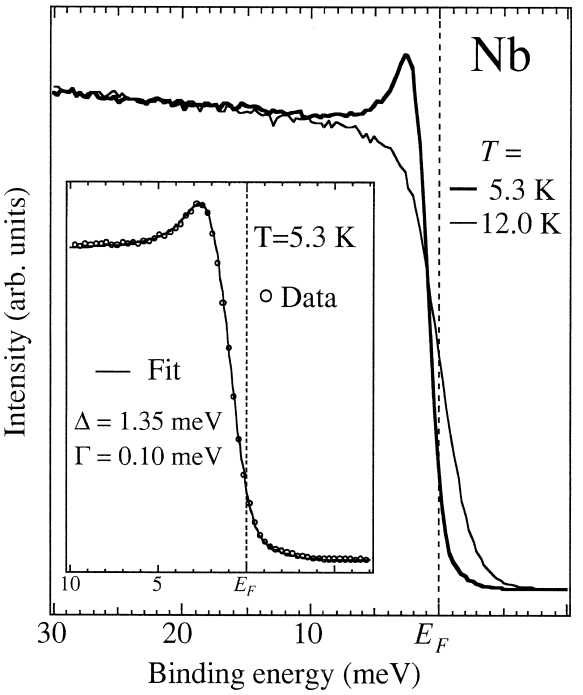

Fig. 2. Ultrahigh-resolution photoemission spectra of Nb measured at 5.3 K (superconducting state) and 12.0 K (normal state). Inset shows Dynes function fits to the peak and the leading edge performed to estimate the superconducting gap value.

known from thermodynamic measurements—3.8 for Nb and 4.5 for Pb [2].

The Dynes function fit deviates from experiment at binding energies beyond the peak, particularly for Pb. This is more clearly seen when we enlarge the superconducting-state spectra and contrast it with that of Nb spectra as shown in Fig. 4. We see in the Pb spectrum: (i) the peak in the superconducting spectrum is itself asymmetrically broadened on the higher binding energy side (4–6 meV) compared to Nb, (ii) a weak feature at about 9 meV, (iii) a dip at 10–15 meV, and a hump around 20 meV. It is known from neutron scattering studies [10] and from a strong-coupling analysis of the tunneling spectra [1,9] that Pb exhibits a transverse phonon at 4.4 meV and a longitudinal phonon at 8.5 meV, and we attribute the features seen in photoemission also to the same origin. For Nb, though the spectral modification is not so spectacular, we see a weak feature around 15 meV, whose energy position matches that of a phonon structure observed from neutron scatter-

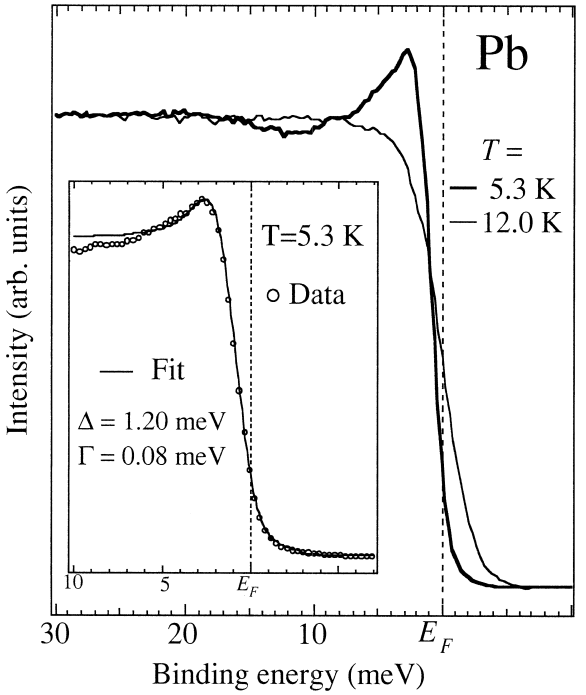

Fig. 3. Ultrahigh-resolution photoemission spectra of Pb measured at 5.3 K (superconducting state) and 12.0 K (normal state). Inset shows Dynes function fits to the peak and the leading edge performed to estimate the superconducting gap value.

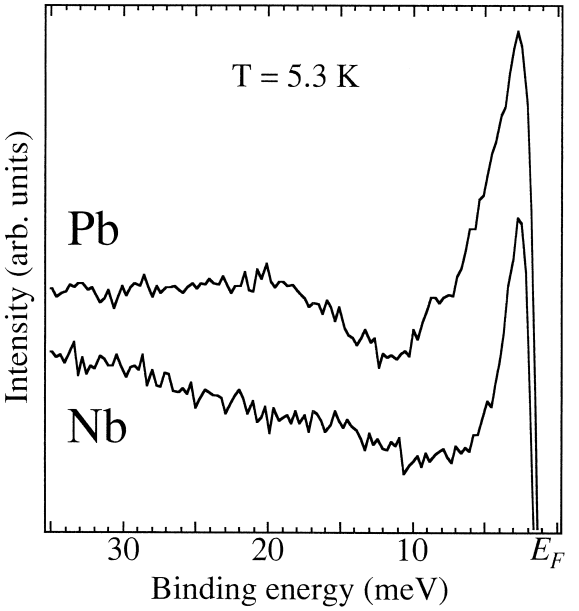

Fig. 4. Comparison of enlarged photoemission spectra of Nb and Pb at 5.3 K shown in order to see the details in the superconducting-state spectra.

ing [11]. We believe these spectral differences are due to the weaker coupling in Nb compared to Pb, which is well known from thermodynamic measurements [2].

For the cuprate superconductors, strong coupling has been established between the collective resonance mode observed at wave vector (π,π) by neutron scattering [12] and the resonance peak–dip–hump lineshape observed at $(\pi, 0)$ in angle-resolved PES [13,14]. Our results show that the peak–dip–hump structure is also observed in a low-T_c system and is thus a characteristic of strong-coupling superconducting transitions.

4. Photoemission results of Ni borocarbides: evidence for anisotropic s-wave in YNi_2B_2C

One can study the anisotropy of a superconducting gap most directly using ARPES. But, materials which can be studied using ARPES are limited since it needs clean and flat surfaces. Also it is difficult to distinguish a d-wave gap from a highly anisotropic s-wave gap, since ARPES do not detect the sign of the order parameter. Here, we show that angle-integrated photoemission can be used for distinguishing anisotropic gaps with the aid of theoretical predictions that the change in anisotropy as a function of impurity is qualitatively different for the d-wave and anisotropic s-wave gaps [15]. For Ni borocarbides, there has been a lot of experimental evidence for the anisotropy of the superconducting gap [16–19], leaving further experimental investigation to address whether the order parameter of YNi_2B_2C is a d-wave or a highly anisotropic s-wave.

Fig. 5 shows ultrahigh-resolution photoemission spectra in the vicinity of E_F for YNi_2B_2C and $Y(Ni_{0.8}Pt_{0.2})_2B_2C$ measured at 6 and 20 K, which were normalized for area under the curve from 25 to −15 meV binding energy. The residual resistivity ratio estimated from resistivity measurements is 37.4 for $x=0.0$ and 2.6 for $x=0.2$ [7]. This indicates that substitution of Ni for Pt introduces impurities as well as changing T_c, which can be qualitatively explained by variations in the DOS at E_F as determined by

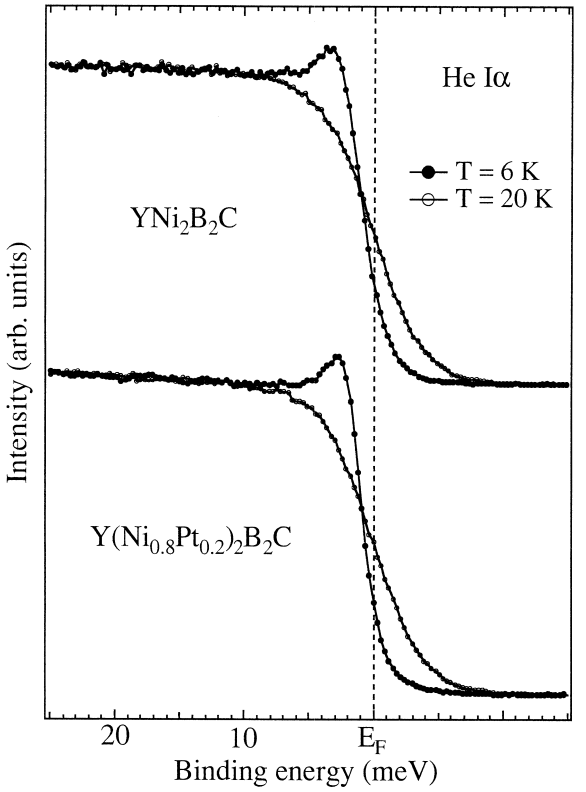

Fig. 5. Ultrahigh-resolution photoemission spectra in the vicinity of E_F of YNi_2B_2C (upper panel) and $Y(Ni_{0.8}Pt_{0.2})_2B_2C$ (lower panel) measured at 6 K (superconducting state) and 20 K (normal state).

specific heat measurements [7]. In the spectra, it is clearly seen that each spectrum shows a peak and a shift of leading edge, characteristic of opening of the superconducting gap. In addition, we note small enhancement of intensity around 7 meV binding energy in $x=0.0$ spectrum, which coincides with the phonon structure reported by neutron scattering measurements [20].

In Fig. 6, we enlarge and compare the superconducting spectra of $x=0.0$ and 0.2, highlighting the small differences between the two compounds. One can notice that the slope of the leading edge is different; the slope is more gentle in $x=0.0$ than in $x=0.2$. This difference is not due to a change in energy resolution and/or position of E_F, because we checked the resolution and the position of E_F just before and after the measurements and confirmed that they remain the same within an error of less than

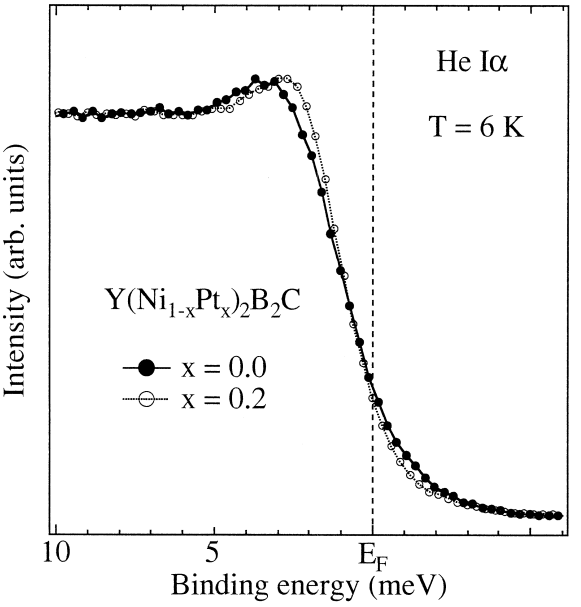

Fig. 6. Enlarged superconducting-state spectra of YNi_2B_2C and $Y(Ni_{0.8}Pt_{0.2})_2B_2C$. There is a small but significant difference in the slope of the leading edge.

± 0.1 and ± 0.05 meV, respectively. Thus the raw data itself give evidence for an interesting change in the shape of the superconducting gap with substitution.

To gain further insight into the shape of the superconducting gap, we carried out numerical calculations with the BCS (isotropic s-wave) function and the Dynes function [8] with gap anisotropy, taking a constant normal state DOS near E_F (Fig. 7). We find that the s-wave function fails to reproduce the shape of the experimental spectra due to its large coherent peak intensity and steep edge, so we just fit the position of the coherent peak using $\Delta=2.5\pm0.2$ meV for $x=0.0$ and $\Delta=1.8\pm0.2$ meV for $x=0.2$. We notice that the slopes of the leading edge of the two calculations are almost parallel (Fig. 7(a)), in sharp contrast to the experimental results (Fig. 6). This implies that the difference in the slope observed experimentally cannot be explained by a difference in the magnitude of the gap alone. Then we tried to fit using the anisotropic Dynes function, which has a gap form of $\Delta_{min}+(\Delta_{max}-\Delta_{min})\cos 2\theta$ (θ is the polar angle in the plane) and a damping factor Γ. For $x=0.0$, if we use a larger Δ_{min} value, we need to use

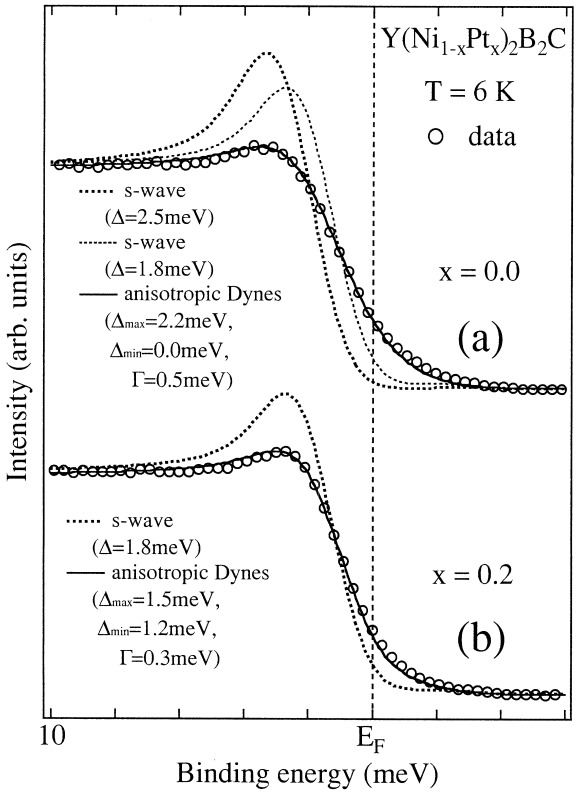

Fig. 7. Examples of numerical calculation results for $x=0.0$ (a) and $x=0.2$ (b) using the isotropic s-wave (dotted lines) and anisotropic Dynes (full lines) functions together with the superconducting-state spectra of YNi_2B_2C and $Y(Ni_{0.8}Pt_{0.2})_2B_2C$ (open circles).

a larger Γ value, giving a worse fit to the leading edge and peak. We find $\Delta_{max}=2.2\pm0.2$ meV, $\Delta_{min}=0.0\pm0.2$ meV, and $\Gamma=0.5\pm0.2$ meV give a reasonable fit, as shown in Fig. 7(a). This agrees with the NMR study [16] and the analysis of the upper critical field data [19], both of which used a d-wave function to explain the data. For $x=0.2$ (Fig. 7(b)) we need to use $\Delta_{max}=1.5\pm0.2$ meV, $\Delta_{min}=1.2\pm0.2$ meV, and $\Gamma=0.3\pm0.2$ meV. As deduced from the numerical calculations, the spectral difference observed in the raw data indicates the change in anisotropy of the superconducting gap: an anisotropic gap in $x=0.0$ and an almost isotropic gap in $x=0.2$. The information we obtain from the present PE study is consistent with recent low temperature specific heat measurements under magnetic field, where γ changes from $H^{1/2}$- to H-dependence on introducing impurities into the crystal [7].

According to theories [14], introducing impurities into an anisotropic s-wave superconductor smears out its anisotropy, resulting in a more isotropic superconducting gap. This is not the case for the d-wave gap, where impurities just increase the DOS at E_F without changing its anisotropy. Since most magnetic measurements have shown antiferromagnetic fluctuations for Ni borocarbides [17], the possibility of a p-wave order parameter, which is expected to be induced by ferromagnetic fluctuation, is small. The present photoemission results have shown a highly anisotropic gap in $x=0.0$ and an almost isotropic gap in $x=0.2$, providing direct evidence for a highly anisotropic s-wave gap, and not a d-wave gap, in Ni borocarbides.

5. Summary

Using ultrahigh-resolution photoemission spectroscopy as a probe to study the strong-coupling superconducting transitions in low-T_c superconductors Pb and Nb, we obtain the following results: the spectra exhibit a peak due to pile-up in the spectra and discrete loss features due to phonons in the superconducting phase, a dip and hump feature, and a temperature-dependent gap with systematic redistribution of spectral weight. On the other hand, comparative study of the superconducting gaps of YNi_2B_2C and $Y(Ni_{0.8}Pt_{0.2})_2B_2C$ have been successfully studied using ultrahigh-resolution PE spectroscopy. A small but important difference in spectral shape is observed and can be attributed to the change in anisotropy of the superconducting gap between $x=0.0$ and 0.2 compounds. This is consistent with recent transport measurements and provides direct evidence for an anisotropic s-wave gap in YNi_2B_2C. Photoemission spectroscopy is thus shown to be a useful and reliable technique to probe single-particle DOS even at very low energy scales. The present study opens up possibilities for studying phase transitions occurring at lower temperatures.

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