Ultrahigh-Resolution Photoemission Spectroscopy of Ni Borocarbides: Direct Observation of the Superconducting Gap and a Change in Gap Anisotropy by Impurity

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We have performed ultrahigh-resolution photoemission spectroscopy of $Y(Ni_{1-x}Pt_x)_2B_2C$ ($x = 0.0$ and 0.2) in order to study the changes in the density of states across the superconducting transition. Because of a drastic increase in energy resolution, we clearly observe the opening of superconducting gaps across T_c in both compounds. Furthermore, we find a small but significant difference in the superconducting-state spectral shape. This can be explained in terms of reduction in gap anisotropy by introducing impurities and provides spectroscopic evidence for an anisotropic s-wave gap in YNi_2B_2C.

PACS numbers: 74.62.Dh, 74.25.Jb, 74.70.Dd

The mechanism of superconductivity in Ni borocarbides which exhibit relatively high critical temperatures (T_c's up to ~ 17 K) [1,2] is a topic of current interest. From a T_c versus γ plot, Carter *et al.* have concluded dominantly phonon-mediated electron pairing as in the A15 compounds [3]. Band structure calculations have also attributed the superconductivity to an electron-phonon mechanism [4–6], which often results in an isotropic s-wave superconducting gap (SG). On the other hand, electrical resistivity shows T^2 dependence implying strong electron correlations in the borocarbides [1]. Photoemission (PE) spectroscopy has shown that the main contribution to the density of states (DOS) at the Fermi level (E_F) is due to Ni 3d electrons with substantial electron correlations (on-site $U \sim 4$–5 eV) [7,8]. Electron correlation is believed to play a role in unconventional superconductivity and can lead to a highly anisotropic SG [9]. Examples of anisotropic gaps are the high temperature superconductors (d-wave) [10], Sr_2RuO_4 (p-wave) [11], etc. It is expected that an isotropic s-wave gap gives an activation-type temperature dependence to the physical properties. However, observed results for the borocarbides are not consistent with this expectation. For example, $\log C/\gamma T_c$ versus T_c/T deviates from exponential behavior [3]. Nuclear magnetic resonance (NMR) studies have shown T^3 dependence of the nuclear relaxation rate $1/T_1$ just below T_c [12] as well as absence of the Hebel-Slichter peak [12,13], reminiscent of results from d-wave superconductors. Moreover, magnetic field dependence of the low-temperature specific heat shows marked deviation from the H linear dependence expected for conventional superconductors and is found to obey a $H^{1/2}$ dependence, suggesting the presence of line nodes on the Fermi surface (FS) [14]. The possibility of d-wave superconductivity has been discussed from an analysis of the upper critical field data using a weak coupling d-wave model [15]. The

SG of the Ni borocarbides is thus believed to be highly anisotropic, leaving further experimental study to clarify whether it possesses an anisotropic s-wave or d-wave order parameter. Since the gap symmetry relates to the mechanism of superconductivity, it is urgent to settle this issue.

Several phase sensitive experiments have been proposed to distinguish between anisotropic s-wave and d-wave in the study of the high temperature superconductors. One of the methods involves a change in the electronic structure of the SG by introducing impurities [16,17]. Such changes have been observed from the low-temperature specific heat measurements under magnetic field for borocarbides [18]. However, further experimental confirmation by different techniques would be necessary to yield a universal description. In this regard, PE spectroscopy is desirable since it measures the electronic structure of the SG *directly*. Unfortunately, PE study of the SG of the borocarbides itself has not been reported until now, since the energy resolution has not been high enough to detect the gap having a smaller energy scale.

In this Letter we show the first PE study of the SG 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 $x = 0.2$). Prior to this study, we constructed a PE spectrometer with highest resolution of 1.5 meV which is comparable to or even smaller than the expected magnitude of the SG, $\Delta \sim 1.7 k_B T_c = 2.2$ meV for YNi_2B_2C. This unprecedented energy resolution has enabled us to detect the SG of these materials as well as small differences in spectral shape. Numerical calculations show that the observed difference can be explained by a change in anisotropy of the SG. The results indicate an anisotropic s-wave gap for YNi_2B_2C.

Single crystals of $Y(Ni_{1-x}Pt_x)_2B_2C$ were grown by a floating zone method [19]. Magnetic susceptibility measurements were performed to confirm the superconducting

T_c's. The residual resistivity ratio estimated from resistivity measurements is 37.4 for $x = 0.0$ and 2.6 for $x = 0.2$ [18]. This indicates that substitution of Ni for Pt introduces impurities as well as changes T_c, which can be qualitatively explained by variations in the DOS at E_F as determined by specific heat measurements [18].

PE measurements were performed on a spectrometer built using a Scienta SES2002 electron analyzer and a GAMMADATA high-flux discharging lamp with a toroidal grating monochromator. The total energy resolution (analyzer and light) using He Iα resonance line was set to 2.0 meV in order to obtain reasonable count rates. The sample temperature was estimated using two silicon-diode sensors mounted at the root and end of a copper extension rod connected to the end of a flowing liquid He refrigerator. The base pressure of the spectrometer was better than 5×10^{-11} Torr. Samples were scraped *in situ* with a diamond file to obtain clean surfaces every 180 min and spectra were obtained after ensuring thermal equilibration of samples. We did not see any spectral changes near E_F within the time interval, indicating the observed spectra are reflecting intrinsic electronic structures. Temperature dependent spectral changes were confirmed by cycling temperature across T_c. By measuring two samples for each compound in three different experimental runs, we have confirmed that all the results shown here are reproducible including that of the leading-edge spectral shape. 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.

Figure 1 shows ultrahigh-resolution PE spectra in the vicinity of E_F for YNi$_2$B$_2$C and Y(Ni$_{0.8}$Pt$_{0.2}$)$_2$B$_2$C measured at 6 and 20 K. The spectra of superconducting and normal states were normalized for the area under the curve from 25 to -15 meV binding energy. At 20 K, well above T_c, the spectrum of YNi$_2$B$_2$C shows a Fermi edge whose midpoint is located at E_F, as expected from the Fermi Dirac (FD) distribution. In contrast, at 6 K, well below T_c, the spectral intensity at and above E_F decreases with a drastic increase at 3.4 meV binding energy, resulting in a sharp peak. Consequently, the leading edge of the spectrum shifts to higher binding energy. These spectral changes cannot be explained by changes in the FD distribution as a function of temperature and unambiguously indicate the opening of a SG below T_c. The intensity at 25 and -15 meV of the two spectra match very well, indicating spectral-weight conservation through T_c, as expected from BCS function. Similar spectral changes are also observed for Y(Ni$_{0.8}$Pt$_{0.2}$)$_2$B$_2$C (Fig. 1, lower panel), indicating the opening of a SG.

The overall spectral shape in superconducting states being similar, there are small differences between the two compounds. To highlight the difference, we enlarge the near E_F spectra at 6 K as shown in Fig. 2. One can notice that the positions of the superconducting coherent peak are different: 3.4 meV for $x = 0.0$ and 2.9 meV for $x = 0.2$.
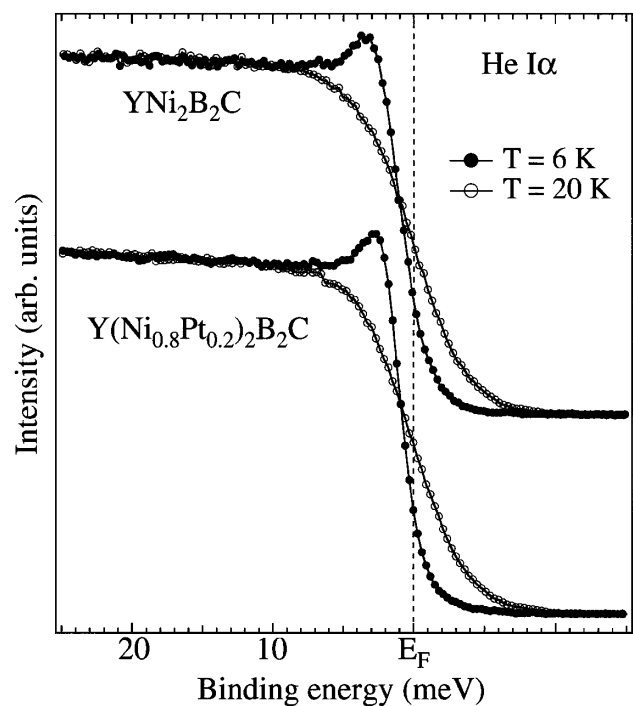

FIG. 1. Ultrahigh-resolution PE spectra in the vicinity of E_F of YNi$_2$B$_2$C (upper panel) and Y(Ni$_{0.8}$Pt$_{0.2}$)$_2$B$_2$C (lower panel) measured at 6 K (superconducting state, ●) and 20 K (normal state, ○). Note that the spectra of 6 K for both compounds clearly show a sharp peak just below E_F and a shift of leading edge to higher binding energy, indicating opening of SG.

This can be attributed to the difference of T_c's since the ratio of the positions 3.4 meV/2.9 meV $= 1.2$ is similar to the ratio of T_c's, 15.4 K/12.1 K $= 1.27$. However, in spite of the difference in the position, the shift of the leading-edge midpoint is nearly the same (0.79 meV for $x = 0.0$ and 0.77 meV for $x = 0.2$). This is because the slope of the leading edge is different: the slope is gentler
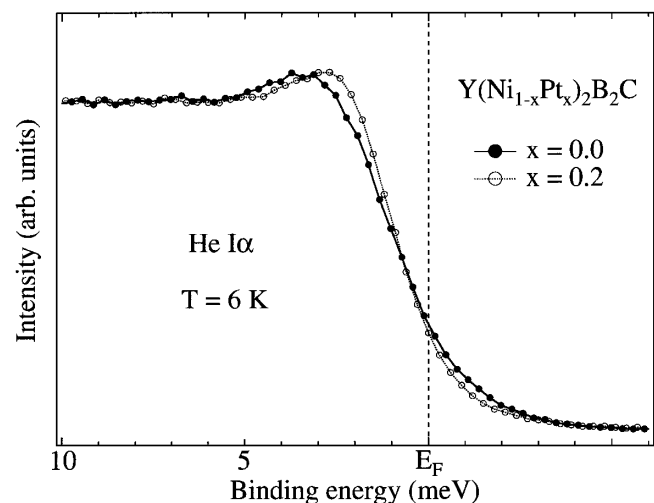

FIG. 2. Enlarged superconducting-state spectra of YNi$_2$B$_2$C (●) and Y(Ni$_{0.8}$Pt$_{0.2}$)$_2$B$_2$C (·⊙·). There is a small but significant difference in the slope of the leading edge.

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 they remain the same within an error of less than ± 0.1 and ± 0.05 meV, respectively. Thus the raw data give evidence for an interesting change in the shape of the SG with substitution. 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].

To gain further insight into the shape of the SG, we performed numerical calculations with the BCS (isotropic s-wave) function and the Dynes function [21] with gap anisotropy, taking a constant normal state DOS near E_F (Fig. 3). 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 by using $\Delta = 2.5 \pm 0.2$ meV for $x = 0.0$ and $\Delta = 1.8 \pm 0.2$ meV for $x =$

FIG. 3. Examples of numerical calculation results for $x = 0.0$ (a) and $x = 0.2$ (b) using the isotropic s-wave (······) and anisotropic Dynes (———) functions together with the superconducting-state spectra of YNi_2B_2C and $Y(Ni_{0.8}Pt_{0.2})_2B_2C$ (○). The isotropic s-wave result for $x = 0.2$ (– – –) is also shown in (a) for comparison. Gold spectrum (○) is shown with a FD function of 6 K convolved by a Gaussian of FWHM of 2.0 meV.

0.2. We notice that the slopes of the leading edge of the two calculations are almost parallel [Fig. 3(a)], in sharp contrast to the experimental results (Fig. 2). 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 a larger Γ value, giving a worse fit to the leading edge and peak. We find $\Delta_{max} = 2.2 \pm 0.2$ meV, $\Delta_{min} = 0.0 \pm 0.2$ meV, and $\Gamma = 0.5 \pm 0.2$ meV give a reasonable fit [22], as shown in Fig. 3(a). This agrees with the NMR study [12] and the analysis of the upper critical field data [15], both of which used a d-wave function to explain the data. For $x = 0.2$ [Fig. 3(b)] we need to use $\Delta_{max} = 1.5 \pm 0.2$ meV, $\Delta_{min} = 1.2 \pm 0.2$ meV, and $\Gamma = 0.3 \pm 0.2$ meV. Here we note that Γ is not due to an extrinsic effect such as a Lorentzian broadening due to the experimental resolution. The experimental resolution is obtained by fitting the data of gold to the FD function convolved by a Gaussian of full width at half maximum (FWHM) $= 2.0$ meV giving an excellent fit to the data, as shown in Fig. 3(c). As deduced from the numerical calculations, the spectral difference observed in the raw data indicates the change in anisotropy of the SG: an anisotropic gap in $x = 0.0$ and an almost isotropic gap in $x = 0.2$. Here we emphasize again that the obtained spectral difference is intrinsic, representing a difference of the electronic structures, since we have measured two samples in different experimental runs and found the experimental results reproducible, as long as we have clean surfaces and ensure thermal equilibration. 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 [18]. Detailed $\log C/\gamma T_c$ versus T_c/T plots also show T^3 and thermally activated behavior for $x = 0.0$ and 0.2 compounds, respectively [23].

Besides the gap anisotropy within one FS sheet, we have to think of the anisotropy between FS sheets. Indeed, the FS of YNi_2B_2C consists of four sheets as reported from a band calculation [24]. The gap value of one of the sheets reported by de Haas–van Alphen measurements has been found to be very small compared to the value obtained by other experimental techniques [25]. But this sheet is a small electron pocket with a volume of 0.3% of the first Brillouin zone and is not expected to influence the total DOS significantly, as is already mentioned in the literature. Moreover, we realized that one of the four FS sheets, forming a cylindrical-like sheet at the X point, has the biggest volume [24], providing a dominant contribution to the DOS. It is plausible to think that the obtained gap anisotropy is occurring in this FS sheet. Furthermore, from a band calculation of YPt_2B_2C using lattice constants of $Y(Ni_{0.8}Pt_{0.2})_2B_2C$, we find that the shape and
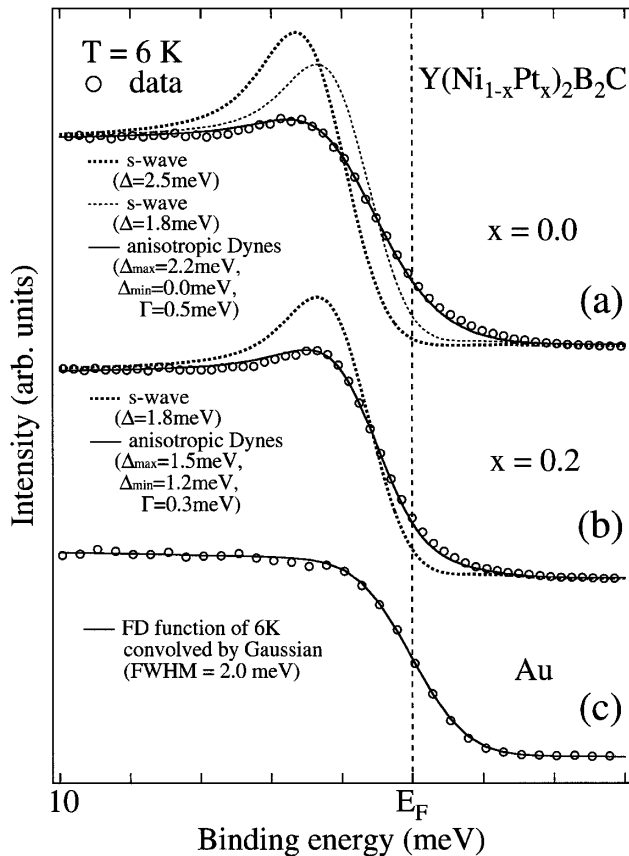
volume of this FS sheet remains similar upon substitution [26]. This indicates that the dominant contribution to the change in gap anisotropy comes from introducing impurities and not a change in electronic structure. According to theories [16,17], introducing impurities into an anisotropic s-wave superconductor smears out its anisotropy, resulting in a more isotropic SG. This is not the case for d-wave SG, where impurities just increase the DOS at E_F without changing its anisotropy. Since most magnetic measurements have shown antiferromagnetic fluctuations for Ni borocarbides [13,27–29], the possibility of a p-wave order parameter, which is expected to be induced by ferromagnetic fluctuation, is small. The present PE 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.

Theoretically, anisotropy can come from (1) momentum(k)-dependent interaction potential and (2) an anisotropic electronic structure, both of which are assumed constant for simplicity in the BCS theory [30]. An anisotropic FS sheet for the borocarbides is known from band structure calculations [6,24,26]. Furthermore, a two-dimensional angular correlation of electron-positron annihilation study of LuNi$_2$B$_2$C has experimentally determined the FS and the authors insist that one of the FS sheets shows nesting behavior [31], which may change the interaction potential along a particular direction. We conjecture that characteristic electronic structures occurring in this material are responsible for the large anisotropy of the gap.

In summary, the SG's of YNi$_2$B$_2$C and Y(Ni$_{0.8}$Pt$_{0.2}$)$_2$B$_2$C 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 SG 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$_2$B$_2$C.

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