Negative isotope effect of a BCS-like gap; an inelastic light scattering study

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In a prior study of the boron isotope effect on the transition temperature (Tc) of RNi2B2C (R = Y, Lu) system, a positive isotope effect was observed, e.g., Tc(+1B) > Tc(+11B). BCS theory predicts that the superconducting gap at zero temperature (Δ0) is proportional to Tc. Therefore, the gap should also show a positive boron isotope effect. On the contrary, in an inelastic light scattering study, we report a negative boron isotope effect on the energy Ω of the gap-like feature in B2g symmetry, e.g., Ω(+1B) < Ω(+11B). The origin of the effect is discussed in terms of selective probing of a non-conventional electron-phonon interaction on part of the Fermi surface, probably near the X point in the Brillouin zone.

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In a previous study of an isotope effect on the transition temperature (Tc) of RNi2B2C (R = Y, Lu) system,1 positive isotope exponents αB = +0.21 ± 0.07 for YNi2B2C and +0.11 ± 0.05 for LuNi2B2C were observed upon changing the mass of the boron site. The exponent αTc is defined as αTc ≡ −ΔlnTc/ΔlnMc. A relatively large positive value despite the light mass of boron is regarded as a good indication that these materials are BCS-type superconductors, where phonons involving boron atoms play a major role in the pairing mechanism.

BCS-type theory predicts that the superconducting gap in the limit of the absolute zero temperature (Δ0) is proportional to Tc. In weak coupling Δ0 = 1.76kBTc, where kB is the Boltzmann constant. The gap should also show a positive isotope effect upon changing the boron mass. We report here the contrary result: In an inelastic light scattering study, we observe a negative isotope effect of the gap-like Raman peak in B2g symmetry.

The gap Δ can be measured by electronic Raman scattering. The photon scattering process excites two quasi-particles out of the condensate at a minimum energy cost of 2Δ. In the limit of small wave-vector transfer q relative to the inverse coherence length and small elastic and inelastic scattering rate relative to 2Δ/ℏ and with neglect of final state interactions, the Raman spectrum has a peak at an energy shift of 2Δ. Earlier measurements on NbSe2 and A15 compounds showed redistribution of the continuum of the Raman spectra and the formation of a 2Δ-like peak upon cooling the samples below Tc.2 Electronic Raman studies have played important role in characterizing the nature of the superconducting gap of the high-temperature superconductors.3

Compared with other techniques that measure the gap, such as tunneling and photoemission spectroscopy, inelastic visible light scattering has the advantage of measuring the anisotropy of the gap while being less surface sensitive.

The single crystal samples were grown by the flux-growth method1,4 and were characterized by resistivity, magnetization, and neutron scattering.5 RNi2B2C crystallizes in the tetragonal body-centered space group I4/mmm, and phononic Raman analyses have been made earlier.6 Here, we concentrate on the electronic Raman scattering from the quasi-particles in normal and superconducting states.

Raman spectra were obtained in a pseudo-backscattering geometry using a custom-made subtractive triple-grating spectrometer designed for very small Raman shifts and ultra low intensities.8 A 3 mW beam of 6471 Å Kr-ion laser light was focused onto a spot of 100 × 100 μm2. The temperature rise ∆T of the focal spot above ambient temperature was estimated by solving the heat-diffusion equation. ∆T is largest at lowest temperature because of the smaller values of the thermal conductivity.6 The estimated ∆T is 2.7K at 4K and 0.9K at 14K for YNi2B2C single crystals. The ambient temperature at which the Raman continua begin to show the redistribution was determined to be 14K, in agreement with this estimate. The spectra were corrected for the Bose factor and therefore are proportional to the imaginary part of the Raman susceptibility.

The “B2g spectra” and “B1g spectra” presented below are actually from the linearly-polarized light scattering geometries of XY (B2g + A2g) and X’Y’ (B1g + A2g), respectively. The A2g contribution to these spectra was determined from the sum of XY and X’Y’ spectra minus the spectrum obtained in LR (B1g + B2g) circularly-polarized scattering geometry. A2g was found to be negligible.
Figure 1 shows the electronic Raman spectra in $B_{2g}$ and $B_{1g}$ geometries of (a) YNi$_2$B$_2$C ($^{10}$B) and (b) LuNi$_2$B$_2$C ($^{10}$B) in the superconducting state (6 K) and normal state (16 K). The figure clearly shows $2\Delta$-like peaks in the superconducting states. As reported earlier,[10] the development of the $2\Delta$-like peaks is indeed due to superconductivity, following the BCS prediction of the gap-vs-temperature very well.[11]

The gap values extrapolated to $T = 0$ are $2\Delta_0(B_{2g}) = 5.0$ meV ($2\Delta_0/kT_c = 3.7$) and $2\Delta_0(B_{1g}) = 6.1$ meV ($2\Delta_0/kT_c = 4.5$) for YNi$_2$B$_2$C, while $2\Delta_0(B_{2g}) = 6.2$ meV ($2\Delta_0/kT_c = 4.5$) and $2\Delta_0(B_{1g}) = 6.6$ meV ($2\Delta_0/kT_c = 4.8$) for LuNi$_2$B$_2$C. Finite scattering intensity below the gap-like peaks is observed even at 6 K. Possibility of signal from the normal-state phase is ruled out and is discussed in our earlier paper[10] in more detail.

We have measured YNi$_2^{10}$B$_2$C (B10-Y), YNi$_2^{11}$B$_2$C (B11-Y), LuNi$_2^{10}$B$_2$C (B10-Lu), and LuNi$_2^{11}$B$_2$C (B11-Lu) single crystals in order to investigate the isotope effect on the “$2\Delta$-like” peaks. Measurements were repeated on 3-4 different single crystals of each set, and comparisons between the two isotopes were made under conditions that were as identical as possible. For instance, one sample of B10-Y and another one of B11-Y were loaded together into the same cryostat and measured several times in the sequence of B10 - B11 - B10 - B11 - B10... in one experimental run.

Figure 2 shows the isotope dependence of the “$2\Delta$-like” peaks at 6 K in various scattering geometries for YNi$_2$B$_2$C and $B_{2g}$ geometry for LuNi$_2$B$_2$C. Clearly, we observe that the $B_{2g}$ peak position in B10-Y is at smaller wavenumber than in B11-Y (Fig. 2a). This behavior was observed in 3-4 pairs of B10-Y and B11-Y. For LuNi$_2$B$_2$C the trend is far less obvious due to weaker signal-to-noise ratio (Fig. 2b). In other scattering geometries (Fig. 2c,d), no such isotope dependence is observed. On the contrary, the $B_{1g}$ peak tends to show a positive isotope effect, but the greater breadth of the peak hinders determining an isotope effect within experimental resolution.

In our earlier paper,[10] it was shown that the $B_{2g}$ peak follows the BCS prediction for the temperature dependence of the superconducting gap. However, as seen in Fig.2a, it does not follow the BCS prediction for the isotope dependence of the gap. Rather, the $B_{2g}$ peak frequency in YNi$_2$B$_2$C, as well as the leading edge of the peak, exhibits a negative isotope effect. There are prior reports of some of these experimental results.[12]

We found empirically that in the region of the $2\Delta$ peaks the ratio of $B_{2g}$ to $B_{1g}$ Raman intensities can be fit to a Lorentzian expression

$$\frac{I_{B_{2g}}}{I_{B_{1g}}} = \frac{A}{(\omega - \omega_0)^2 + \Gamma^2},$$

near the ‘gap-like’ peak frequency, $\omega_0$. Figure 2 shows the results of fitting the above equation to the ratio of the $B_{2g}$ to $B_{1g}$ spectra. The fit is excellent around the peak and below, deviating much at higher frequencies. No such fit is possible for $I_{B_{2g}}$ or $I_{B_{1g}}$ itself. From the fits to several sets of $B_{2g}/B_{1g}$ Raman ratios, we obtained the isotope effect exponent due to boron, $\alpha_B^{\text{Raman}} = -0.32 \pm 0.03$ for YNi$_2$B$_2$C and $-0.04 \pm 0.07$ for LuNi$_2$B$_2$C, where $\alpha_B^{\text{Raman}} \equiv -\frac{\Delta \ln I}{\Delta \ln M_B}$. $M_B$ is the mass of the boron isotopes. Since there is little evidence for an isotope effect in the $B_{1g}$ spectra, we attribute these results for $\alpha_B^{\text{Raman}}$ primarily to the negative isotope effect on the $B_{2g}$ spectrum.
negative isotope effect of the superconducting gap. Negatively, the isotope effect would have to be much smaller and possibly positive on those parts of the Fermi surface probed in $A_{1g}$ and $B_{1g}$ Raman geometries.

There is a simple picture of the electronic structure that may give a strong clue to where the $B_{2g}$ vertex is large. According to the band structure calculations for LuNi$_2$B$_2$C and YNi$_2$B$_2$C, there is a flat band that may cross the Fermi surface near the X point [wave-vector given by $(\pi/a, \pi/a, 0)$] if there is a small change in parameters. This band has strong anti-bonding $d_d\sigma$ interactions as well as $d_{z2}$ character on Ni sites. If we take a nearest neighbor, planar, Ni-Ni tight binding model with coupling $t$, we obtain a band dispersion $\varepsilon(k) = 4t\cos(k_xa/2)\cos(k_ya/2)$. This has a saddle point at X. A good starting approximation to the Raman vertex is the so-called mass approximation, valid when the photon energy is less than that of all inter-band transitions starting or ending at the Fermi energy. It says that the $B_{2g}$ Raman vertex is proportional to $\partial^2\varepsilon/\partial k_x \partial k_y$. For the assumed band structure, this would give $\partial^2\varepsilon/\partial k_x \partial k_y = 4t(a/a)^2\sin(k_xa/2)\sin(k_ya/2)$, which takes on its maximum value at the X point.

It would be useful to verify this suggestion with a band structure calculation of the mass vertex of the band that crosses the Fermi energy near the X point. The next step would be to study the coupling between this band and the boron phonon modes. There is one such calculation in the literature, which emphasizes the role of the $A_{1g}$ zone center boron mode on modulating the angle of the B-Ni-Ni tetrahedra. However, much more needs to be done, with a particular look for novel couplings that would give a negative isotope effect on the gap associated with this band.

The superconducting gap of borocarbides will not be as simple as calculated by BCS theory. The finite intensity below the gap observed in our Raman measurements (Figs. 1 and 2) and$^9$ of superconducting $RNi_2B_2C$ ($R = Y$, Lu) system are good indications of the complex nature.

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**Figure 3:** Ratios of $B_{2g}$ to $B_{1g}$ intensities and the fit. Fitting (fine solid lines) of the intensity ratio of the $B_{2g}$ spectra to the $B_1$ the co shown the fit.

**Figure 4:** Plot of $B_{2g}$ peak frequencies ($\Omega$) at 6K and the onset temperatures of the superconducting transition of six different YNi$_2$B$_2$C single crystals. The dashed line on the plot represents BCS prediction $2\Delta_0 = 3.52k_BT_c$. We have measured the superconducting transition temperatures using a SQUID magnetometer and eliminated the possibility that the particular B10 samples in our study have lower $T_c$ values than those of B11 samples. Figure 3 shows a plot of $B_{2g}$ peak frequencies ($\Omega$) at 6K and the onset temperatures of the superconducting transition of six different YNi$_2$B$_2$C single crystals. As is clearly seen, B11-Y samples do have larger $B_{2g}$ peak frequencies than B10-Y samples, in contradiction to the BCS prediction. This figure shows that the isotope effect of the $B_{2g}$ peak frequencies is negatively correlated with the isotope effect of the $T_c$ in YNi$_2$B$_2$C. The dashed line on the plot represents $2\Delta_0 = 3.52k_BT_c$, the BCS prediction in the weak coupling limit.

There is no previous report known to us of an observed negative isotope effect of the superconducting gap. Negative isotope effects have been observed for the transition temperatures of the Pd-H(D) system and undoped YBa$_2$Cu$_3$O$_{7-\delta}$. In the following discussion we assume that the $B_{2g}$ peak is directly due to superconducting gap $2\Delta$. How, then, can we explain a negative isotope effect for the gap measured in $B_{2g}$ Raman symmetry along with a positive isotope effect for $T_c$ and small or zero isotope effects for the gap measured in $B_{1g}$ and $A_{1g}$ symmetries?
of the gap of borocarbide superconductors.

In conclusion, we observed a negative boron isotope effect of the gap-like feature in $B_2g$ electronic Raman spectra from $YNi_2B_2C$ single crystals. For $LuNi_2B_2C$, the negative isotope effect is weaker, and may be zero within our experimental resolution. A likely explanation is that the $B_2g$ Raman vertex selectively probes those portions of the Fermi surface which show a negative boron-isotope effect of the order parameter in the superconducting state. We have suggested that this may occur at the X point, the corner of the Brillouin zone in the basal plane.

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