Optical Conductivity of the Superconductors $L\mathrm{Ni}_2\mathrm{B}_2\mathrm{C}$ (L = Lu and Y)

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We have measured the optical reflectivity of $\mathrm{LuNi}_2\mathrm{B}_2\mathrm{C}$ and $\mathrm{YNi}_2\mathrm{B}_2\mathrm{C}$ compounds, and have evaluated the optical conductivity both below and above the superconducting transition temperature. The normal state optical properties suggest that these superconductors are almost in the clean limit. Our results below T_c give, however, evidence of a superconducting gap signature, and are in agreement with a BCS singlet ground state. Our experimental findings also indicate a moderate-to-strong coupling limit for the pairing mechanism. [S0031-9007(96)02060-1]

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The discovery [1–3] of superconductivity at relatively high temperatures in the new family of quaternary intermetallic compounds $L\mathrm{Ni}_2\mathrm{B}_2\mathrm{C}$ (L = Lu, Tm, Er, Ho, Dy, Y) has motivated intensive experimental study of these materials. Initial characterization of these systems has revealed several interesting and potentially intriguing properties: the striking layeredlike crystallographic similarity of the $L\mathrm{Ni}_2\mathrm{B}_2\mathrm{C}$ compound with the cuprate-oxide superconductors [4], and the fact that superconductivity is observed not only for the nonmagnetic rare earth elements but also for the heavy magnetic rare earths Tm, Er, Ho, and Dy [1,3]. This obviously raised the expectation for the occurrence of a variety of phenomena associated with the competition between magnetism and superconductivity [5] and led to speculation that some exotic pairing mechanism is responsible for their relatively high T_c's.

While the superconducting state properties have been well characterized by transport and magnetic measurements [1–3,5–7], the mechanism of superconductivity still remains to be settled. In this respect, an important intrinsic parameter is the superconducting energy gap. The determination of such a relevant energy scale has important implications in connection with the possible excitations and the strength of the coupling mechanism (electron-phonon or electron-electron), which mediates superconductivity. In this work, we present our first attempts to detect the superconducting gap by optical means on the $L\mathrm{Ni}_2\mathrm{B}_2\mathrm{C}$ series. Here we concentrate our attention on the Lu (T_c = 16.6 K) and Y (T_c = 15.6 K) compounds. Optical spectroscopic methods are revealed to be a powerful experimental tool, which allows us to find the optical signature of the gap, suggesting BCS-like superconductivity in the moderate-to-strong coupling limit.

The Y-polycrystalline and the Lu-single crystal samples used in the present experiment were prepared following the method described in detail by Cava *et al.* [1] and Cho *et al.* [7]. The optical properties were obtained by measuring the reflectivity $R(\omega)$ (for the Lu-single crystal, $R(\omega)$ corresponds to the *ab*-plane) as a function of temperature between 15 and 10^5 cm^{-1}, using four different spectrometers [8]. By performing the Kramers-Kronig transformation with standard high frequency extrapolations, we obtain the complete set of optical properties expressed in terms of the complete optical conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ [8]. The data for the Y compound were, moreover, completed above 12 eV by the measurement up to 50 eV of Widder *et al.* [9]. In the normal state, $R(\omega)$ was extended from 15 cm^{-1} down to dc by means of the Hagen-Rubens (HR) extrapolation, using dc-conductivity (σ_{dc}) data in agreement with the measured values. Below T_c, $R(\omega)$ at $T > 6$ K was completed with an *"ad hoc"* HR extrapolation for frequencies smaller than 10 cm^{-1} in order to impose a metalliclike behavior (i.e., $R(\omega) \rightarrow 100\%$ for $\omega \rightarrow 0$). At 6 K, since $R(\omega)$ is 100% within the experimental error, we set $R(\omega) = 100\%$ below 15 cm^{-1} down to zero frequency. These extrapolations do not affect $\sigma_1(\omega)$ in the far infrared (FIR) above 15 cm^{-1} [8].

Figure 1(a) displays the measured reflectivity for both the Lu and Y compounds over the complete spectral range at 300 K. The inset shows the temperature dependence of $R(\omega)$ for the Lu compound in FIR. Similar results have also been obtained for the Y compound. Our relative precision, relevant for the temperature dependence, is 0.3%. $R(\omega)$ at 300 K in FIR is Drude-like which indicates a rather conventional metallic behavior. By lowering the temperature from 100 K down to T_c, $R(\omega)$ displays a kind of FIR plasma edge behavior below 150 cm^{-1}, manifested by the shoulder feature at about 60–70 cm^{-1}. Coincident with T_c, there is the onset of another clear temperature dependence: $R(\omega)$ increases with the formation of a plateau, which merges at 100% (i.e., total reflection) at 6 K. The threshold frequencies, above which there is the onset of absorption (i.e., deviation from total reflection) at 6 K, are 45 and 56 cm^{-1} for the Lu and Y (not shown) compounds, respectively.

The equivalence of the experimental results between a polycrystalline and single crystalline sample above

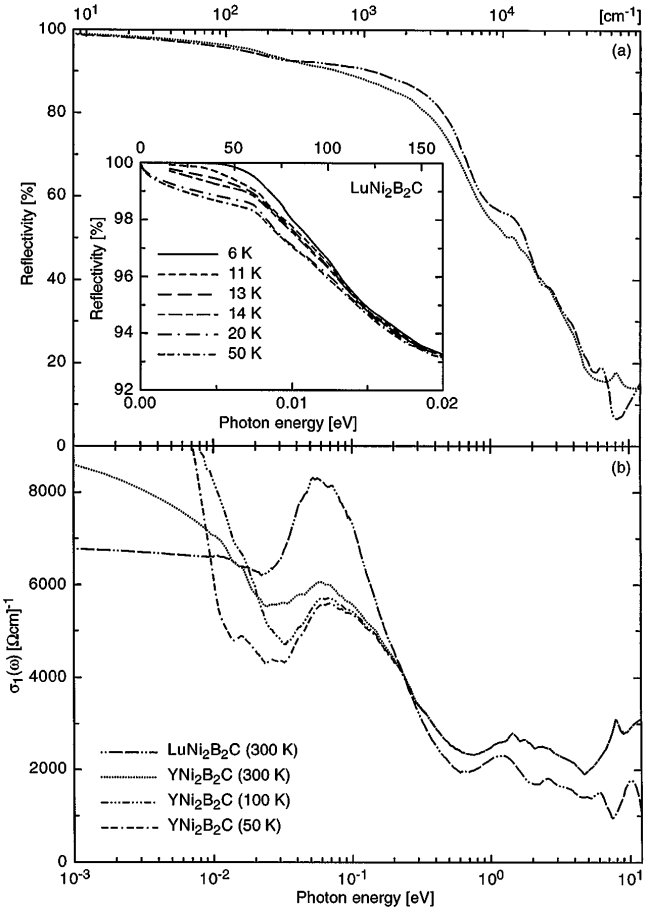

FIG. 1. (a) Reflectivity $R(\omega)$ and (b) real part $\sigma_1(\omega)$ of the optical conductivity at 300 K for the Lu and Y compounds over the whole measured frequency spectral range (logarithmic energy scale). For the Y compound the $\sigma_1(\omega)$ spectra at 50 and 100 K are also displayed. The inset shows the temperature dependence of $R(\omega)$ in FIR for the Lu compound.

and particularly below T_c indicates that the structural anisotropy does not apparently affect the optical response in any significant manner. This is also in accord with the band-structure calculation [10], which suggests that despite their layered structure, these borocarbide compounds are electronically three dimensional and more similar to conventional intermetallic superconductors than to the cuprate high-T_c superconductors, for which an anisotropic optical response was found [11].

In Fig. 1(b), we show the $\sigma_1(\omega)$ spectra at 300 K for both compounds and at 100 and 50 K for the Y compound which are representative of the normal state. Our spectra at 300 K compare rather well with previous optical investigations [9,12]. At high frequencies we observe several absorptions which are ascribed to electronic interband transitions [9,10]. Below the midinfrared (MIR), $\sigma_1(\omega)$ is actually the combination of a metallic Drude-like behavior and of a broad absorption at about 500 cm^{-1}. The total spectral weight encountered by the two components corresponds to a total plasma frequency ω_p of about 4 eV, in agreement with the ω_p estimate on the Y compound in Ref. [9]. This two component picture was also found in the high-T_c cuprates [11] and more recently in the superconducting alkali-metal doped C_{60} fullerenes [8]. Previous investigation [9] also hints at a two component picture. Indeed, even though the two components were not completely revealed (mainly because the FIR spectral range is partially missing), the normal state properties could not be explained by a simple Drude model only [9].

The temperature dependence of the real part of the optical conductivity in FIR is presented in Fig. 2 for both compounds. There is a clear temperature dependence, which bears a striking similarity with the results found for the superconducting alkali-metal doped fullerenes A_3C_{60} [8]. By decreasing the temperature there is first a narrowing of the Drude component in the normal state [Fig. 1(b)] and for temperatures below T_c we find a progressive suppression of the optical conductivity in FIR, which is very reminiscent of the expected scenario for the opening of a gap. Moreover, $\sigma_1(\omega)$ at 11, 13, and 14 K for the Y compound displays a weak feature at about 7 meV which freezes out below 8 K (i.e., when the gap is fully opened). Its appearance is made possible by the narrowing of the metallic component in $\sigma_1(\omega)$ and the opening of the gap. Its origin is yet unclear but a recent inelastic neutron scattering investigation seems to favor a phonon mode excitation for this absorption [13].

As already mentioned, the normal state properties deviate rather remarkably from the simple Drude picture of conventional metal (i.e., scattering rate $\Gamma \sim 1000$ cm^{-1}), for which a less ω-dependent $\sigma_1(\omega)$ is expected in the FIR spectral range. Indeed, a shallow minimum is seen at about 150–200 cm^{-1}, which is basically the consequence of the MIR absorption at 500 cm^{-1}. The careful study of the interplay between the various components in $\sigma_1(\omega)$ at $T > T_c$ is also essential for the forthcoming discussion in terms of a temperature dependent superconducting energy gap at $T < T_c$. We established that the harmonic oscillator associated to the MIR absorption is temperature independent, while the effective metallic contribution undergoes a progressive narrowing, incorporated mainly by a temperature dependent scattering rate Γ [14]. Such a Drude narrowing above T_c could be indicative of the relevant role played by the correlation effect. The effective metallic contribution results then in a narrow Drude component of $\sigma_1(\omega)$ with $\Gamma \sim 40$ cm^{-1} for both compounds at 50 K, which is even smaller than the expected superconducting gap. Only the high frequency tail of the Drude resonance is in the spectral range where the superconducting energy gap should manifest (see Fig. 2). This suggests that the materials are very close to the clean limit. The additional presence of the MIR absorption might lead to another explanation of the data: that the behavior of $\sigma_1(\omega)$ below T_c is due to a type of plasma edge effect, similar to what has been found in the high-T_c cuprates [15,16]. Nevertheless, the onset of the temperature dependence of $R(\omega)$ with T_c and even more importantly, the absence of any zero crossing of the real part of the dielectric

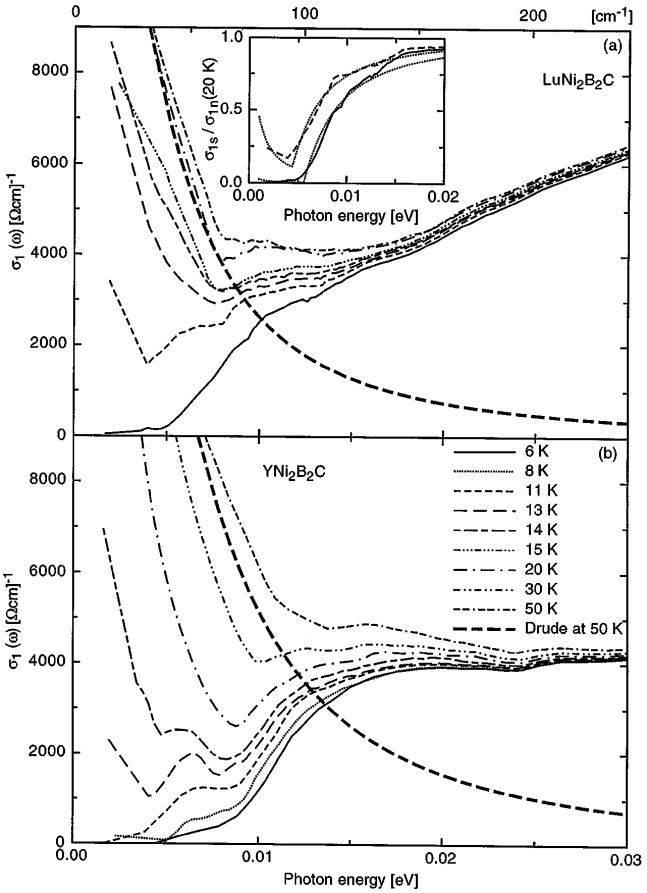

FIG. 2. Temperature dependence of $\sigma_1(\omega)$ in the FIR spectral range for the Lu and Y compounds (note that the legend for the various temperatures is the same for both compounds). The inset displays $\sigma_{1s}(\omega, T)/\sigma_{1n}(\omega, 20\ \mathrm{K})$ at 6 and 11 K for the Lu compound compared with the BCS theory (dot line). We also display the Drude component of the fit at 50 K, obtained with plasma frequency $\omega_p = 5896$ and 7719 cm^{-1}, and scattering rate $\Gamma = 35$ and 44 cm^{-1} for the Lu and Y compounds, respectively.

function $\varepsilon_1(\omega)$ (which would define the screened plasma frequency) in the FIR frequency range, rule out this explanation. Therefore, even though $\Gamma < 2\Delta$, the materials are not yet in the extreme clean limit, which would completely prevent the detection of the gap.

The optical conductivity at 6 K is basically zero up to the threshold frequencies of about 5.6 and 6.9 meV for the Lu and Y compounds, respectively. We ascribe the onset of absorption in $\sigma_1(\omega)$ to the optical identification of the superconducting gap. The gap values correspond to a reduced gap ratio of $2\Delta/k_B T_c \sim 3.9$–5.2. These ratios suggest that the borocarbide superconductors should be placed within the moderate-to-strong coupling limit. This also agrees with the outcome from the previous optical investigation [9], where a rather strong electron-phonon interaction coupling constant of $\lambda_{\mathrm{tr}} \sim 1.2$ was inferred from the normal state properties. Furthermore, the specific heat discontinuity at the superconducting transition in the Lu compound yields a ratio $\Delta C/\gamma T_c \sim 3$, implying strong coupling, as well [17]. The moderate-to-strong coupling limit scenario contrasts, however, with the conclusions drawn from the tunneling investigations [18–20]. Even though the tunneling spectra are consistent with the BCS prediction, the gap ratios range from 2.9–4.2. This variation of results allows for interpretation either within the weak or the moderate-to-strong coupling limit. Such a wide range of possibilities is often explained by the surface sensitivity of the tunneling technique, which might cause alterations of the intrinsic bulk gap value.

The experimental electrodynamic response can be directly compared with the BCS theoretical prediction [21]. The inset of Fig. 2(a) shows the ratio of the superconducting over the normal state optical conductivity $\sigma_{1s}(\omega, T)/\sigma_{1n}(\omega, 20\ \mathrm{K})$ for the Lu compound at 6 and 11 K. There is an excellent agreement between experiment and theory, suggesting that $L\mathrm{Ni}_2\mathrm{B}_2\mathrm{C}$ are BCS-like superconductors. Moreover, the functional form also reflects the so-called case II coherence factors [22], which depend sensitively on the symmetry of the superconducting wave function. Therefore, the agreement between theory and experiment gives evidence for a singlet ground state. The analysis of the experimental data in terms of the BCS approach allows us to extract the temperature dependence of the order parameter $\Delta(T)$, shown in Fig. 3(a). The agreement with the BCS prediction is satisfactory, though in the moderate-to-strong coupling limit. However, close to T_c the error bars associated to the determination of $\Delta(T)$ are quite large. The observation of the superconducting gap would suggest that, strictly speaking, these materials are not in the so-called extreme clean limit, where the mean free path ℓ exceeds the coherence length ξ. This issue is often the subject of acute controversy [11]. The question of whether the clean or dirty limit applies is based on the assumption that a simple Drude response accounts for the conductivity in the metallic state. We have shown above, as is evident from Figs. 1 and 2, that $\sigma_1(\omega)$ cannot be described by the simple Drude model alone.

Moreover, one can apply a sum rule or spectral weight argument in order to obtain an initial estimate of the penetration depth $\lambda(T)$ [8]. Figure 3(b) shows the temperature dependence of λ evaluated from the missing spectral weight in $\sigma_1(\omega)$ [i.e., by integrating $\sigma_1(\omega)$ between 10 and 800 cm^{-1}] due to the opening of the gap. For the Y compound, $\lambda(T)$ follows very closely the empirical "two fluid" model (λ_{tf}) which is a good approximation of the extreme anomalous BCS limit (λ_∞) [22]. Such a temperature dependence deviates quite remarkably from the London model (λ_L), which seems to be appropriate for the Lu compound [Fig. 3(b)]. The London limit for the Lu compound would enforce the scenario of superconductivity very close to the clean limit, which is more likely to be realized in a single crystal. In the polycrystalline sample λ might be enhanced by grain size effects. At 6 K, where the gap is fully opened, we obtain an estimate for $\lambda(0)$ of 4.8×10^{-5} cm

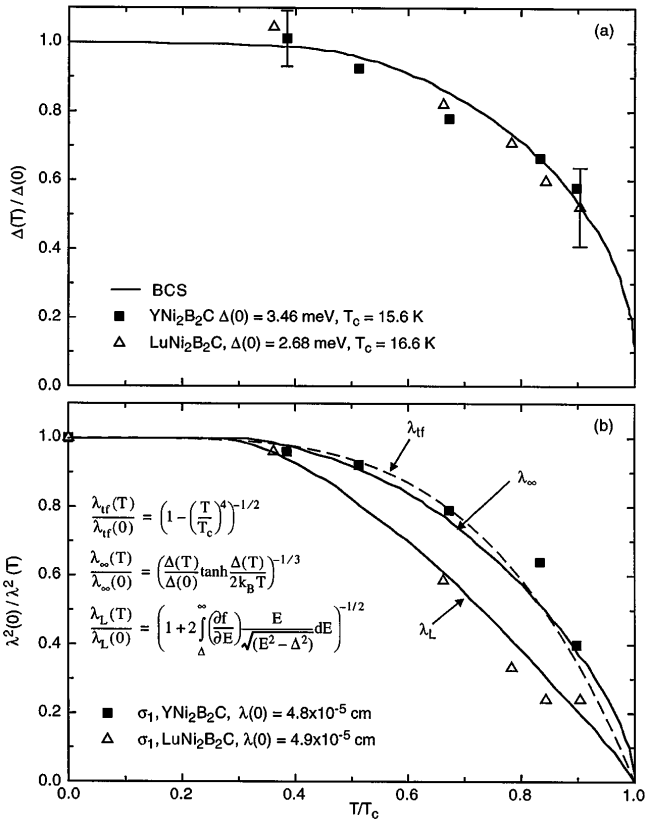

FIG. 3. Temperature dependence of the superconducting energy gap Δ (a) and of the penetration depth λ (b) for both compounds, compared with the BCS prediction (λ_∞), the London model (λ_L), and the two fluid approach (λ_{tf}).

and 4.9×10^{-5} cm for the Y and Lu compounds, respectively. Our $\lambda(0)$ values are five times larger than the values obtained from μSR measurements [23] and from upper and lower critical magnetic field studies [6] for the Y and Lu compounds, respectively. This latter disagreement may partially originate, from the optical point of view, in the underestimation of the spectral weight below the FIR spectral range (i.e., beyond our measurable low frequency limit), as consequence of the HR-like extrapolation we have performed for $T < T_c$ [8], and also in the spectral range around the onset of the 500 cm^{-1} absorption.

In summary, our first attempts to optically investigate the electrodynamic response of the borocarbide superconductors allows us to establish that the Lu and Y compounds are very close to the clean limit, showing nevertheless the optical signature for the opening of a gap below T_c. The data are consistent with the BCS scenario in the moderate-to-strong coupling limit. This would suggest that the relevant excitation responsible for the superconductivity pairing might be associated with low frequency phonon modes (e.g., optical phonons [9]). In this respect, calculation within an Eliashberg formalism [8], where a realistic phonon spectrum [24] can be considered, is highly desirable.

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