Specific Heat Measurement of the Layered Nitride Superconductor Li_xZrNCl

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Specific heat has been investigated in a layered nitride superconductor, $Li_{0.12}ZrNCl$, with $T_c = 12.7$ K. The obtained data have shown a marked dichotomy: The specific heat jump at T_c ($\Delta C/\gamma_n T_c = 1.8$) and the superconducting gap ratio ($2\Delta/k_B T_c = 4.6$–5.2) have indicated an intermediate to a strong coupling of electrons, while the upper limit of the electron-phonon coupling constant λ has directly been estimated to be 0.22, which belongs to a weak coupling regime. Furthermore, the rapid increase of γ as a function of magnetic field suggests that the present material has an anisotropic s wave gap.

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The recent discovery [1] of superconductivity of MgB_2 with $T_c = 39$ K has fueled a renewed interest in the research of superconductors without a strong electron correlation. Examples of such superconductors are electron-doped β-HfNCl and β-ZrNCl [2,3], whose maximum T_c values are 25.5 and 15 K, respectively. These materials have layered crystal structures where Hf-N (or Zr-N) double honeycomb layers are sandwiched by Cl bilayers. Electron doping is achieved by Li intercalation into the van der Waals gap of the Cl bilayers. According to band calculations [4–6], doped electrons are accommodated into a two-dimensional (2D) band, which is derived mainly from Hf $5d$ (or Zr $4d$) orbitals that hybridize with N $2p$ orbitals. One of the unique properties of these systems is the small density of states at the Fermi level [$N^*(0)$] for their high T_c, as revealed by a recent magnetic susceptibility measurement [7] of Hf compounds. The band calculations [4–6] also suggest a small $N^*(0)$ as well as a 1 order of magnitude smaller value of the Hopfield parameter [$= N^*(0) \times \langle I^2 \rangle$, where I represents the electron-phonon matrix element] than is expected for materials with a similar value of T_c. On the other hand, a recent tunneling spectroscopy measurement [8] has revealed a markedly large superconducting gap ratio $2\Delta/k_B T_c = 5.0$–5.6, which can be viewed as a fingerprint of a strong coupling superconductor. Muon spin relaxation (μSR) measurements [9,10] have also suggested that these materials exhibit the correlation of T_c versus 2D superfluid density, which is very similar to those found in cuprates and organics that are widely believed to be exotic superconductors. Very recently, we have found [11] an anomalously small pressure effect on T_c, and an analysis based on McMillan's theory showed that, if the superconductivity in the present system is mediated by phonon alone, the electron-phonon coupling constant (λ) must be larger than 3. To understand these apparently contradicting results of the theories and experiments, we need an unambiguous determination of λ in such a way that various BCS or McMillan relations are not assumed. In this Letter, we report the results of the first specific heat (C) measurement of Li-doped ZrNCl with $T_c = 12.7$ K, and show that λ is less than 0.22. Using this value and McMillan's formula, we cannot reproduce the experimentally observed T_c. This result clearly indicates that some factors that are neglected in McMillan's theory must be taken into account to explain the high T_c of this class of superconductors.

We prepared β-ZrNCl in sealed quartz tubes using a chemical vapor transport technique, following the procedures described in Ref. [12]. Lithium intercalation was carried out using an n-butyl-lithium solution in hexane in an Ar-filled glove box. We examined the sample by synchrotron x-ray radiation at BL02B2, SPring-8, and confirmed that the sample was in a single phase. The intercalated Li content (x) was determined to be 0.12 ± 0.01 by inductively coupled plasma spectroscopy. For magnetization and specific heat measurements, we generated pellets with a high degree of c axis orientation by compressing the powder sample in the glove box. Magnetization and heat capacity measurements were carried out, using a SQUID magnetometer and the physical property measurement system (Quantum Design), respectively, with the configuration of the $H \parallel c$ axis.

To discuss obtained specific heat data, we need information concerning the upper critical field at $T = 0$ K [$H_{c2}(0)$] of the sample. Therefore, we carried out magnetization measurements to determine $H_{c2}(0)$ prior to specific heat measurements. Figure 1(a) shows the temperature dependence of magnetization at various magnetic fields. At $H = 1$ mT, magnetization markedly decreased at approximately 12.5 K, indicating the superconducting transition. As the field increases, however, the transition becomes broader, and the determination of T_c from the raw data becomes more difficult. Therefore, we adopted a scaling analysis to determine T_c values at various magnetic fields, which was previously applied to organics [13] and also to the Hf analogue [14] of the present compound. The result of 2D scaling is shown in the inset of Fig. 1 in the form of $M/(TH)^{1/2}$ vs $[T - T_c(H)]/(TH)^{1/2}$, where $T_c(H)$ is the scaling parameter. Since the analysis is applicable to the temperature region where thermal fluctuation is domi-

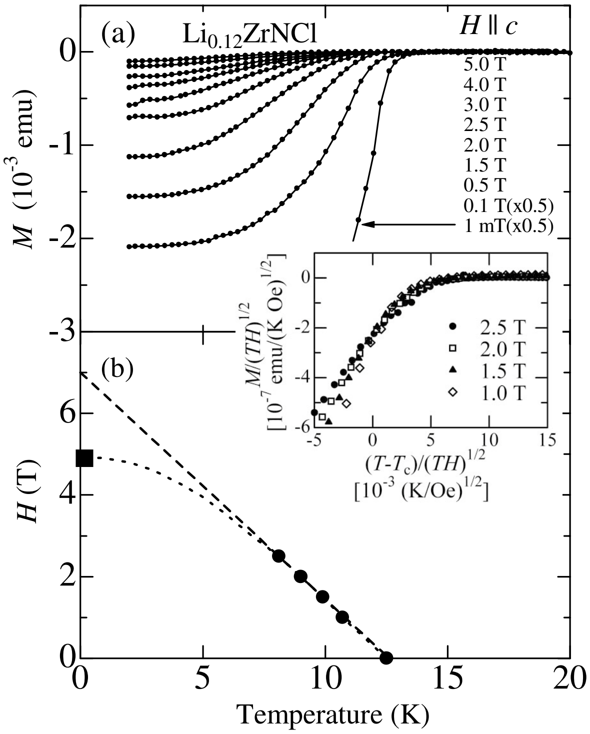

FIG. 1. (a) Temperature dependence of magnetization at various magnetic fields. The values of $H = 0.1$ T and 1 mT are multiplied by 0.5. (b) $T_c(H)$ values determined from scaling analysis are shown as closed circles. A closed square at $T = 0$ K represents $H_{c2}(0)$ calculated using the Werthamer-Helfand-Hohenberg theory. A dashed line is a linear fit to the $T_c(H)$ data. A dotted curve is a guide to the eyes. The inset shows a scaling plot of MT curves.

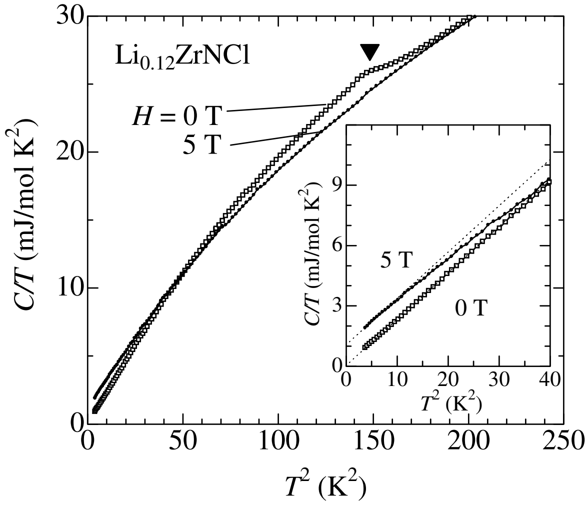

FIG. 2. Specific heat data for $H = 0$ and 5 T presented in the form of C/T versus T^2. A closed triangle indicates the anomaly associated with the superconducting transition. The inset shows the low-temperature behavior, together with linear fits (dashed lines) to the lowest temperature portion of the data.

nant over quantum fluctuation, we used only the data between 1 and 2.5 T in which T_c does not decrease very much from the value at zero magnetic field. Thus determined $T_c(H)$ values are shown in Fig. 1(b), together with the value of the zero field limit (at $H = 1$ mT), as closed circles. Using these values of $T_c(H)$ and the Werthamer-Helfand-Hohenberg theory [15], we estimated $H_{c2}(0)$ to be 5.0 T, which is shown as a closed square in Fig. 1(b). This value is consistent with the $H_{c2}(0)$ value ($= 4.7$ T) for a similar compound ($Li_{0.17}ZrNCl$), which was deduced from another scaling analysis of magnetization data [10]. Analysis of specific heat data also ensures *a posteriori* that 5 T is enough to suppress superconductivity (*vide infra*). Therefore, a slight decrease of magnetization discerned below 8 K for 5 T data in Fig. 1(a) does not represent the bulk property, but should be attributed to some misaligned grains whose c axes are not parallel to the field direction.

In Fig. 2, we plot C/T as a function of T^2 for $H = 0$ T (superconducting state) and 5 T (normal state). A clear anomaly associated with the superconducting transition is discerned at about $T^2 = 150$ K^2 in the 0 T data, as indicated by a closed triangle. At low temperatures, C/T has a slight curvature for both data (perhaps due to a highly anisotropic phonon dispersion in this layered structure), and tends to go to zero and a finite value for $H = 0$ and 5 T, respectively, as absolute zero temperature is approached. In the inset of Fig. 2, a magnified view of the low-temperature behavior is shown. Because of the curvature, we have fitted only the lowest temperature portion of 5 T data to the usual relation of $C/T = \gamma_n + \beta T^2$, which is represented as a dashed line in the inset. This plot gives a value of $\gamma_n = 1.1$ mJ/mol K^2, which is in accord with the result of more complete analysis where the complicated phonon contribution is eliminated, as discussed below.

In Fig. 3, we show heat capacity data in the form of $\Delta\gamma \equiv [C(H, T) - C(H = 5\mathrm{T}, T)]/T$ versus T for several values of H. Here, we have fitted the 5 T data to a polynomial, and used the polynomial in calculating $\Delta\gamma$ to minimize data scattering. In this plot, the H independent lattice contribution is eliminated and only the electronic part is displayed. Therefore, $\Delta\gamma$ represents the difference in the electronic specific heat coefficient between the superconducting state [$\gamma(H, T)$] and the normal state (γ_n). At $H = 0$ T, a jump is clearly observed at the superconducting transition of approximately 12 K. Taking the entropy balance into account, we obtained $T_c = 12.7$ K and $\Delta C/T_c = 1.79$ mJ/mol K^2. As the temperature decreases, $\Delta\gamma$ continuously decreases, and finally saturates below about 3.5 K. This behavior is in accord with the s wave symmetry of the superconducting gap. Indeed, data below 5 K are fitted to a formula $\Delta\gamma = AT^{-5/2} \times \exp(-\frac{\Delta_0}{k_B T}) - \gamma_n$ with $\Delta_0/k_B = 29$ K and $\gamma_n = 1.0$ mJ/(mol K^2), as exemplified in the inset of Fig. 3. We have measured several samples from the same batch, and have found scattering of Δ_0 and γ_n values to be

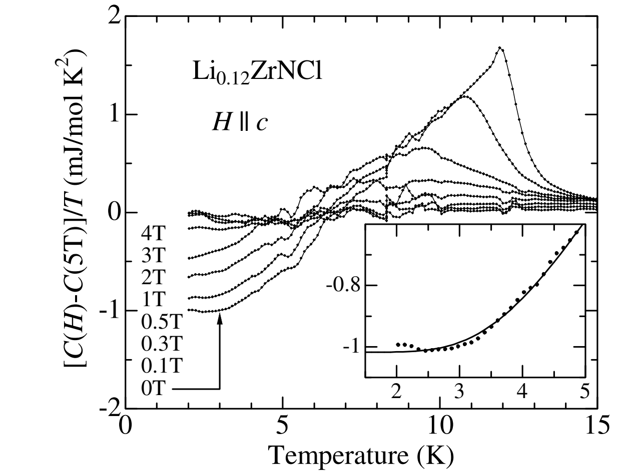

FIG. 3. Temperature dependence of the difference in the electronic specific coefficient between the superconducting state and the normal state for several H values. The inset shows the low-temperature behavior of $H = 0$ T data, together with the fit (solid line).

$\Delta_0/k_B = 29$–33 K and $\gamma_n = 1.0 \pm 0.1$ mJ/mol K^2. These gap values correspond to the ratios of $2\Delta_0/k_BT_c = 4.6$–5.2, which belong to the strong coupling regime, but are slightly smaller than that reported for $Li_{0.5}(THF)_y HfNCl$ by a recent tunneling spectroscopy experiment [8]. As for γ_n, it seems very small for a superconductor with $T_c = 12.7$ K. For example, an oxide superconductor $LiTi_2O_4$ with $T_c = 11.4$ K possesses $\gamma_n = 19.2$ mJ/(mol K^2) [16], which is almost 20 times as large as that of the present material. The normalized specific heat jump at T_c is now expressed as $\Delta C/\gamma_n T_c = 1.8$, which is substantially larger than that expected for a weak coupling limit ($= 1.43$).

As the magnetic field is applied along the c axis, T_c rapidly decreases, and the transition significantly broadens, similar to the case of magnetization. At low enough fields, however, we can barely determine T_c as a function of applied field. Extrapolation of thus obtained $T_c(H)$ data to $T = 0$ K yields the $H_{c2}(0)$ value of about 2.6 T, which is even smaller than that obtained from the scaling analysis of magnetization data. This fact also ensures the validity of taking 5 T data as a normal state reference. With the application of the magnetic field, low-temperature γ is also restored very rapidly. Finite $\gamma(H)$ at low temperatures should be attributed to field-induced quasiparticles in vortex cores. To observe the evolution of γ with the application of the magnetic field, we plot γ at the lowest temperature in the present measurement ($= 2.0$ K) as a function of H in Fig. 4. γ increases very rapidly with H, and almost reaches the normal state γ_n at 2 T. This result is quite surprising because nearly all the electrons lose the superconducting gap much lower than $H_{c2}(0)$ that is determined to be 5.0 T from magnetization measurements. The rapid restoration of γ has also been observed in the

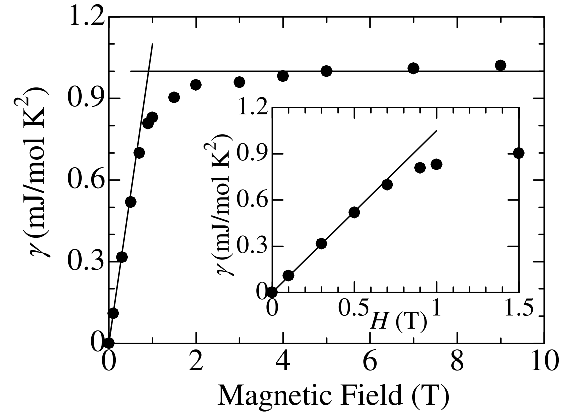

FIG. 4. γ at 2.0 K is shown as a function of H. The inset exemplifies the H linear dependence of γ at fields lower than 0.7 T.

$Ba_{1-x}K_xBiO_3$ system [17], as well as in an unoriented powder sample of MgB_2 [18]. The latter case was later explained [19] by a study using single crystals as being due to the existence of two gaps associated with two bands and their anisotropies. These complex issues are not relevant to the present case since Li_xZrNCl is a single-band system. It should be noted that the γ value shows saturating behavior above 2 T, ensuring again that the superconductivity is, indeed, suppressed by a field of 5 T.

The field dependence of γ at low fields is displayed in an enlarged scale in the inset of Fig. 4. Clearly, γ varies linearly with the magnetic field below 0.7 T. The H linear dependence of γ has been observed in superconductors with an isotropic s wave gap, such as V_3Si and Nb_3Sn [20] or $LiTi_2O_4$ [16], but is distinct from that observed in $LuNi_2B_2C$ (highly anisotropic s wave gap) [21] or $La_{2-x}Sr_xCuO_4$ (d wave gap) [22]. Recently, Nakai *et al.* have theoretically revealed [23] that $\gamma(H)$ shows a crossover from H linear dependence at low fields to $\sqrt{H}$ dependence at high fields in an anisotropic s wave superconductor, and that the linear increase of γ at low fields is more rapid as the degree of anisotropy becomes larger. Therefore, the field dependence of γ suggests that the present superconductor has a highly anisotropic s wave gap. This is an interesting point that deserves to be further investigated by experimental probes such as angle resolved photoemission.

The determination of γ_n ($= 1.0 \pm 0.1$ mJ/mol K^2) allows us to estimate the λ value using the equation $\gamma_n = \frac{2}{3}(1 + \lambda)\pi^2 k_B^2 N^*(0)$ [24]. Here, we assume $N^*(0)$ is the same as the density of states calculated by the band calculation [$N_b(0)$]: We can neglect the effect of small differences in band filling between the present experiment and calculations because of the almost filling independent density of states in this 2D system. When we assume that electron correlation induced mass enhancement of the carriers is negligible, we can take $N^*(0) \approx N_b(0) = 0.19$–$0.26$ states/(eV spin f.u.) [4–6]. The combination of the lower limit of $N^*(0)$ $(= 0.19)$ and the upper limit of γ_n $(= 1.1\ \mathrm{mJ/mol\,K^2})$ yields the upper limit of λ, which is 0.22. If the effect of mass enhancement cannot be neglected, the upper limit of λ would be even smaller. This result strongly indicates that the present superconductor obviously belongs to a weak coupling regime in terms of electron-phonon interaction. When we use McMillan's equation $T_c = (\omega_{\mathrm{ph}}/1.2)\exp[-1.04(1+\lambda)/\{\lambda - \mu^*(1 + 0.62\lambda)\}]$ with the maximum value of λ $(= 0.22)$ and optimal values of ω $(= 700\ \mathrm{cm}^{-1})$ [25] and μ^* $(= 0)$, we obtain T_c of 2.6 K, which is much smaller than the experimentally observed value of 12.7 K.

In a previous paper [11], we have concluded on the basis of an anomalously small pressure effect on T_c that, if the present superconductor is within McMillan's scheme, λ must be larger than 3. As we found in this study, however, the upper limit of λ is about 0.22. Therefore, by combining the results of specific heat and high pressure experiments, we can provide further evidence that McMillan's scheme is not applicable to the present system.

One important point that should be noted is that, while the electron-phonon interaction directly estimated from the normal state γ is small, the effective pairing interaction between electrons must be strong in view of the large superconducting gap ratio and specific heat jump at T_c. This duality suggests that the effective pairing interaction is reinforced by some mechanism(s). Magnetic interaction as extensively discussed in several oxide superconductors would be irrelevant to the present case since the present compound does not contain any magnetic ions. Instead, dynamical correlation among electrons, which is neglected in McMillan's theory but must be present in the Fermi liquid system like the present one, may be one possible candidate for such interaction. Recently, Bill *et al.* have pointed out [26,27] that, in addition to phonon, the acoustic plasmon mode that originates from the dynamical part of Coulomb interaction in layer structured materials may as well contribute to the superconducting pairing interaction, and that T_c, which would otherwise be below 1 K, can be increased to a value similar to an experimentally observed value. The importance of the dynamical part of Coulomb interaction in low-carrier-density systems has been emphasized in several papers [28,29].

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