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Superconductivity in molecule-intercalated Li_xZrNCl with variable interlayer spacing

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Specific heat has been investigated in electron-doped Li_xM_yZrNCl superconductors, in which interlayer spacing d can be controlled by the intercalation of organic molecules M. It has been revealed that, upon enlargement of d by molecule cointercalation, T_c is enhanced concomitantly with the superconducting coupling strength whereas the density of states at the Fermi level is kept almost constant. Structural and spectroscopic analysis proved that the molecules are intercalated without affecting electronic nor vibrational states, simply increasing the interlayer spacing. These results lead us to conclude that the enhancement of T_c is ascribed to the improvement of two dimensionality, which is consistent with a recent theory that discussed superconductivity in a band insulator on a honeycomb lattice with disconnected Fermi surfaces.

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I. INTRODUCTION

Two dimensionality is widely believed to provide a stage in which intriguing superconducting states appear. Cuprates[1] and Fe-based pnictides[2] with layered structure are exemplified as this class of materials since they exhibit high-transition-temperature (high-T_c) superconductivity with an unconventional pairing state. Although the superconducting state has been established to be rather conventional, graphite-intercalated compounds[3,4] and transition-metal dichalcogenides[5] have been extensively studied for more than three decades. Thus far, the effect of two dimensionality on superconductivity has been studied by several experimental techniques, such as searching for new layered superconducting materials and making films with one-unit-cell thickness[6] or with a quantum well structure.[7] However, systematic control of dimensionality is difficult since several intrinsic and/or extrinsic origins affect T_c. The electron-doped layered nitride ZrNCl and HfNCl superconductors[8,9] are candidates to enable systematic control of carrier density and two dimensionality because modulation of the interlayer distance has been demonstrated solely by means of organic molecule intercalation.

Pristine ZrNCl and HfNCl are band insulators with a band gap of 3 eV and 4 eV, respectively. Their crystal structure is composed of alternate stacking of Zr(Hf)-N double honeycomb layers sandwiched by Cl layers along the hexagonal c axis. Alkali metals can be intercalated into the van der Waals gaps between the Cl layers as shown in Fig. 1(a). Electron-type charge carriers are transferred into the Zr(Hf)-N layers from the alkali ions and then, superconductivity with maximum $T_c=15.2$ K and 25.5 K appears for Li_xZrNCl and $Li_x(THF)_yHfNCl$,[9,10] respectively. According to band-structure calculations,[11–15] the conduction band is mainly of $4(5)d$ character of the Zr(Hf) orbitals and the Fermi surface consists of two disconnected, quasi-two-dimensional cylinderlike sheets centered at the corner of hexagonal Brillouin zone, K and K' points. Thus far, several experiments[10,16–20] and theories[13,15] have suggested unusual features, such as a small density of states (DOS) at the Fermi level and a weak electron-phonon interaction for their T_c values. A T_c-x phase diagram was found to be very unique, as shown in Fig. 1(b).[10,18] In the low-doping region, the materials are still insulating without any discernible ordering. With increasing x, superconductivity suddenly appears at $x\sim 0.05$ for Zr and 0.15 for Hf compounds, respectively, indicating the superconductor-insulator (SI) transition. Most interestingly, enhancement of T_c upon reducing carrier density near the verge of the SI transition has been observed only in Zr compounds. Such T_c enhancement toward a band insulator is quite unusual among superconductors. On the other hand, T_c is almost independent of x at $x\gtrsim 0.15$ for both Zr and Hf compounds.

Recently, systematic studies of doping variation in the specific heat and magnetic susceptibility in Li_xZrNCl have revealed that, upon reducing carrier density, the superconducting coupling strength and spin susceptibility are concomitantly enhanced with T_c while the DOS at the Fermi level is kept almost constant, suggesting enhancement of magnetic fluctuations that would be responsible for the pairing interaction with approaching a band insulator upon reducing the carrier density.[19] Furthermore, muon spin-relaxation measurements[20] and specific-heat measurements have revealed that the superconducting order parameter is highly anisotropic, as it has been also suggested theoretically.[21] These experimental and theoretical observations would suggest a possible pairing mediated by magnetic fluctuations, despite the nonmagnetic band insulator nature of the present compounds ZrNCl and HfNCl.

Dimensionality control in the nitride superconductors has been demonstrated by synthesizing Li_xM_yHfNCl, where M represents an organic molecule. Cointercalation of molecules [$M=NH_3$, THF (tetrahydrofuran, C_4H_8O), and PC (propylene carbonate, C_4H_8O)] with Li allows us to control interlayer spacing d and carrier density independently. T_c is enhanced from 20 K in Li_xHfNCl up to 25.5 K in $Li_x(THF)_yHfNCl$ with increasing d with x independence of T_c preserved [see, Fig. 1(b)].[18] It has been discussed that the improvement of nesting condition would be responsible for

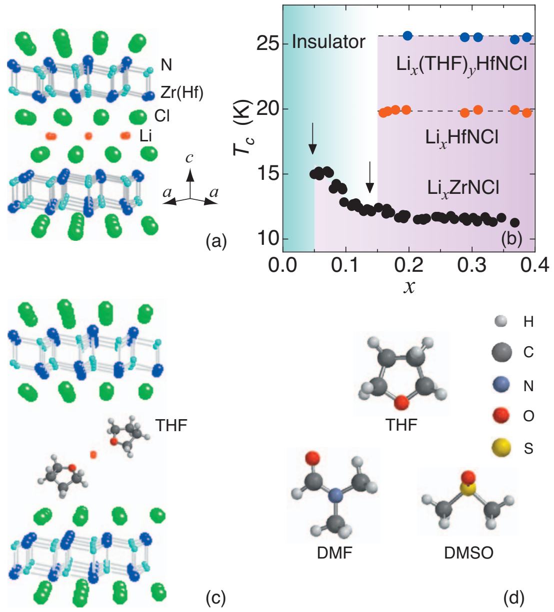

FIG. 1. (Color) (a) Crystal structure of $\mathrm{Li}_x\mathrm{Zr(Hf)NCl}$. (b) Doping variation in T_c for $\mathrm{Li}_x\mathrm{ZrNCl}$, $\mathrm{Li}_x\mathrm{HfNCl}$, and $\mathrm{Li}_x(\mathrm{THF})_y\mathrm{HfNCl}$ (data points are taken from Refs. 10 and 18). (c) Crystal structure of organic molecule-intercalated $\mathrm{Li}_xM_y\mathrm{Zr(Hf)NCl}$. (d) Schematic figure of DMF and DMSO molecules used in this study. THF molecule is also shown. In (b), arrows represent the doping region where the magnetization measurements were performed in the present work. In (c), THF molecules are shown as an example.

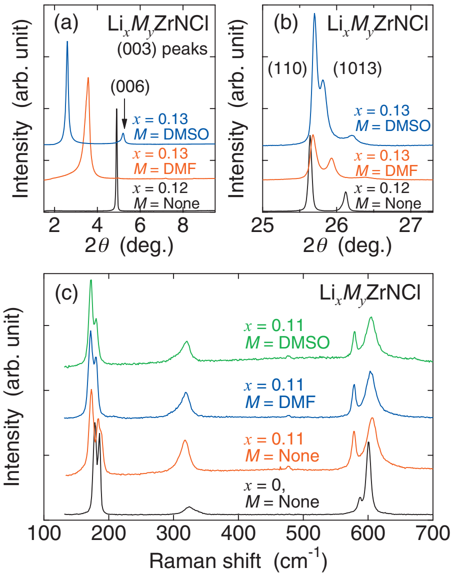

FIG. 2. (Color) (a) (0 0 3), (b) (1 1 0), and (1 0 13) reflection peaks of the synchrotron x-ray diffraction pattern for $\mathrm{Li}_xM_y\mathrm{ZrNCl}$ samples, taken at BL02B2, SPring-8. (c) Raman-scattering spectra for the pristine compound (ZrNCl) and $\mathrm{Li}_{0.11}M_y\mathrm{NCl}$.

pairing interaction of electrons. However, the origin of the T_c enhancement is still unclear since there has been no systematic study of the d variation in physical properties, mostly due to extreme air sensitivity of the Hf compounds. The Zr system can also form molecule-intercalated phases[22,23] and it has been confirmed that thermodynamic measurements can be performed without degradation of the samples.

In this paper, we present the results of the specific-heat measurements for a series of $\mathrm{Li}_xM_y\mathrm{ZrNCl}$ superconductors. Details of the sample synthesis and measurements are described in the next section. We will show the experimental results in Sec. III and discuss the effects of molecule intercalation on the physical properties in Sec. IV. Upon the intercalation of organic molecules, T_c was kept at a constant value in the low-doping region but was enhanced in the higher doping region. We found that superconducting coupling strength is concomitantly enhanced with T_c whereas the density of states was kept almost constant upon the enlargement of the interlayer spacing. These results exhibit good agreement with the latest theory that predicted a magnetic fluctuation mediated pairing in the present compound. We will then summarize this paper in Sec. V.

II. EXPERIMENTS

Pristine β-ZrNCl powders were prepared by a chemical vapor transport method.[8] Obtained powders showed a green pale color. As reported in Ref. 18 for the Hf analog, we performed Li and molecule intercalation separately. Li intercalation was carried out by dispersing pristine powders into n-BuLi/hexane solution with an appropriate molarity for the intended doping level x for one day. After separation from the solvent, cointercalation of organic molecules was performed by dispersing the Li-intercalated powders into the organic solvents, that is, DMF [(N,N)-dimethylformamide, $\mathrm{C_3H_7NO}$] and DMSO [dimethyl sulfoxide, $\mathrm{(CH_3)_2SO}$] [see, Fig. 1(d) for their molecular structure]. Both Li and molecule intercalation were performed in an Ar filled glove box. The actual Li and molecular content, x and y, were determined from the final product of $\mathrm{Li}_xM_y\mathrm{ZrNCl}$ powders within an accuracy of ± 0.01 by inductively coupled plasma spectroscopy, and carbon and sulfur analyzer, respectively, at the analytical research core for advanced materials, IMR, Tohoku University. The ratio of y/x was found to be approximately 2 and 3 for DMF and DMSO, respectively. X-ray diffraction measurements were performed using sealed

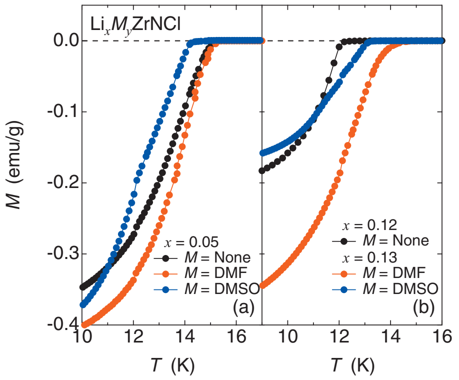

FIG. 3. (Color) Magnetization taken at a field of 10 Oe as a function of temperature, T, for $\mathrm{Li}_xM_y\mathrm{ZrNCl}$ with (a) $x=0.05$ and (b) $x=0.13$. In (b), for Li-intercalated compounds without molecules, x value is 0.12.

samples in glass fiber capillaries at the synchrotron-radiation source, BL02B2, SPring-8. The wavelength of the incident beam was 0.80270(1) Å (15.2 keV). Raman-scattering spectra were recorded using an excitation wavelength of 532 nm.

Magnetization measurements were performed using a superconducting quantum interference device magnetometer. Specific-heat measurements were carried out by a relaxation method. For specific-heat measurements, we prepared c axis oriented pellets with 2.5 mm diameter and 0.5 mm thickness by compressing the powders. The c axis misorientation was revealed to be less than 5° by x-ray rocking curve measurements.[16,18,19,24] The magnetic field $\boldsymbol{H}$ was applied along the c axis ($\boldsymbol{H} \parallel c$) in all the measurements.

Figures 2(a) and 2(b) show synchrotron x-ray diffraction pattern for the samples with DMF and DMSO molecules and with a Li content of $x=0.13$. The diffraction angle 2θ of the out-of-plane (0 0 3) peaks dramatically changed after molecule intercalation, although in-plane (1 1 0) peaks stayed at almost the same position. These results indicate that the interlayer distance d was significantly enlarged by molecule intercalation as demonstrated in the Hf analog.[18,22,23]

Raman-scattering spectra at ambient temperature for pristine ($x=0$) and a series of materials with $x=0.11$ are shown in Fig. 2(c). Five phonon lines were observed above 150 cm^{-1}, which is in agreement with previous reports.[25] All peaks became broader and shifted to lower energy after Li intercalation because of the interaction between phonons and electrons provided by the Li ions. There was no additional peak, and change in line width and energy shift could not be resolved after molecule intercalation for both DMF and DMSO molecules, indicating that contribution from organic molecules themselves is negligibly small. Moreover, these results imply that the existence of organic molecules do not affect the charge transfer from Li ions to Zr-N layers and the resultant interaction between electrons and phonons at least at the Γ point of the Brillouin zone. Therefore, we can conclude that cointercalation of organic molecules with Li enlarges the interlayer spacing between the conducting Zr-N layers without changing the electronic states within each layer.

III. RESULTS

Figures 3(a) and 3(b) show the temperature (T) dependence of the magnetization for Li$_x$$M_y$ZrNCl with $x=0.05$ and 0.13, respectively. T_c values in the samples before molecule intercalation were 15 K at $x=0.05$ and 12.2 K at $x=0.13$, respectively. At $x=0.05$, T_c was unchanged for $M=$DMF but was lowered for $M=$DMSO. On the other hand, at $x=0.13$, T_c was enhanced by the intercalation of both DMF and DMSO molecules.

To see the effect of molecule intercalation more clearly, we plotted T_c as a function of interlayer distance d in Fig. 4. Below $d=13$ Å, a remarkable difference was found in the d dependence of T_c between the two distinct doping regions. As shown in Fig. 1(b), a Li content of $x=0.05$ is located on the verge of the SI transition and T_c decreases with increasing x. In contrast, T_c becomes almost x independent with further doping by $x \gtrsim 0.13$. At $x=0.05$, T_c was almost constant with respect to molecule intercalation but was increased with increasing d at $x=0.13$. With further enlargement of the interlayer spacing ($d \gtrsim 13$ Å), T_c slightly decreased for both $x=0.05$ and 0.13. d dependence of T_c at $x=0.13$ is qualitatively reminiscent of that observed in a previous study of Hf compounds, although no doping variation has been observed, which is in contrast to Zr compounds [see, Figs. 1(b) and 8(a)].[18] Therefore, in the low-doping region near the verge of the SI transition, T_c variation in Zr compounds is considerably anomalous among layered nitride superconductors, not only for doping but also for interlayer spacing.

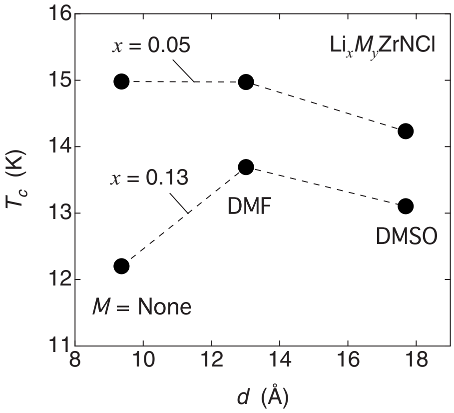

FIG. 4. T_c variation as a function of the interlayer distance, d, for Li$_x$$M_y$ZrNCl with $x=0.05$ and 0.13.

Figures 5(a)–5(c) show T dependence of the electronic part of the specific heat (C) divided by T, $\Delta C/T$, for Li$_{0.12}$ZrNCl, and Li$_{0.13}$$M_y$ZrNCl with DMF and DMSO molecules, respectively. Here, we focused on the materials with $x \sim 0.13$ since x and d dependence of T_c exhibited common features between Zr and Hf compounds, as mentioned above. The electronic part of the specific heat can be estimated as $\Delta C(H,T) \equiv [C(H,T) - C(H > H_{c2},T)]$, where H_{c2} is the upper critical field for the $\boldsymbol{H} \parallel c$ configuration.[17,19] H_{c2} was determined by the scaling analysis of the magnetization[17,26] and was found to be ~ 5 T for Li$_{0.12}$ZrNCl (Ref. 17) and also for the molecule-intercalated compounds. The enhancement of T_c by the intercalation can be clearly discerned as in the magnetization measurements, although the jump of $\Delta C/T$ at T_c seems to be relatively broad due to the polycrystalline nature of the specimen. $\Delta C/T$ at the lowest temperature exhibited a similar value, implying that the contribution from the normal electrons is unchanged via molecule intercalation. As the magnetic field was applied along the c axis, the jump of $\Delta C/T$ at T_c was broadened and its magnitude lowered considerably in all of the materials. In contrast, at the lowest temperature of 2 K, the specific heat was already restored to the normal-state value ($\Delta C/T \sim 0$) at 3 T in the compound without molecules but was smaller than zero even at 3 T in the molecule-intercalated compounds. The magnetic field effect will be discussed later.

To make a comparison of C values before and after the molecule intercalation, we will focus on the $\Delta C/T$ data at zero magnetic field. In Fig. 6, the temperature dependence of $\Delta C/T$ is plotted as a function of temperature normalized by T_c, T/T_c (T_c used here was determined from the magnetiza-

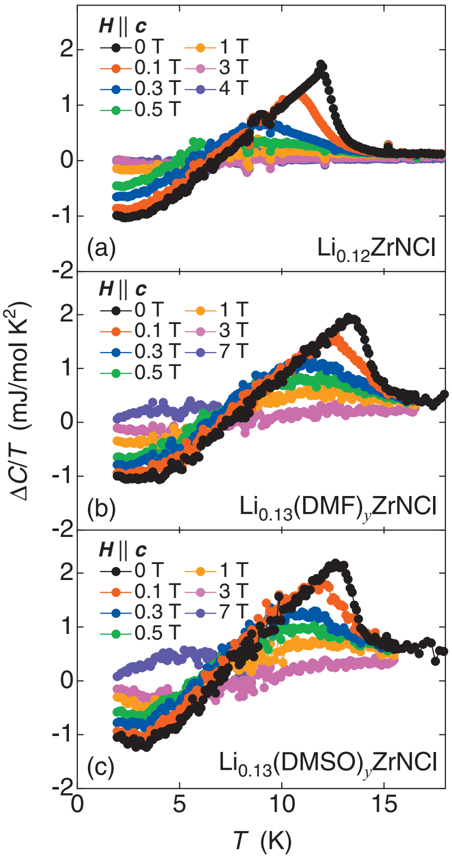

FIG. 5. (Color) Temperature dependence of the electronic part of the specific heat, $\Delta C/T \equiv [C(0\ \mathrm{T}) - C(5\ \mathrm{T} > H_{c2})]/T$, for (a) $\mathrm{Li}_{0.12}M_y\mathrm{ZrNCl}$, and for $\mathrm{Li}_{0.13}M_y\mathrm{ZrNCl}$ with (b) M=DMF and (c) DMSO molecules.

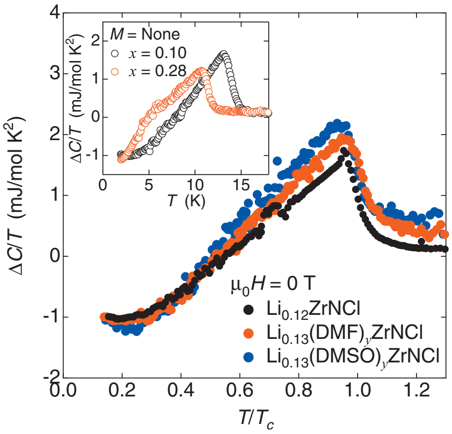

FIG. 6. (Color) Main panel: the electronic part of specific heat $\Delta C/T$ in zero magnetic field as a function of temperatures normalized by T_c, T/T_c, for $\mathrm{Li}_xM_y\mathrm{ZrNCl}$. Inset: $\Delta C/T$ for $\mathrm{Li}_x\mathrm{ZrNCl}$ with x=0.10 and 0.28.

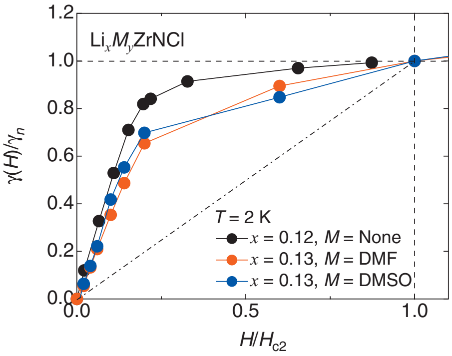

FIG. 7. (Color) Normalized electronic specific-heat coefficient, $\gamma(H)/\gamma_n$, at 2 K as a function of the magnetic field normalized by H_{c2}, H/H_{c2}. The dashed-dotted line represents an H-linear dependence, which is expected in superconductors with an isotropic gap.

tion measurements as shown in Fig. 3). In this plot, the normal-state Sommerfeld constant γ_n can be estimated as $\gamma_n \equiv -\Delta C/T(T \to 0, H=0)$. At high temperatures near the transition, $\Delta C/T$ for molecule-intercalated compounds are apparently higher than that for Li-intercalated compounds without molecules and then, the jump at T_c is broadened. These results imply enhanced fluctuation effects due to the improvement of two dimensionality. Despite of the polycrystalline nature of the samples, the magnitude of the jump increases after molecule intercalation, indicating that the coupling strength of the paired electrons is enhanced with increasing d. As clearly seen in Fig. 6, $\Delta C/T$ at the lowest temperature did not changed between before and after molecule intercalation. From this plot, we found that $\gamma_n \sim 1.1$ mJ/mol K^2 in all compounds. Here, we would like to emphasize the x dependence of the specific heat. As shown in the inset of Fig. 6, upon reducing doping from x=0.28 to 0.10, the shape of the entire temperature dependence changed dramatically to convex shape with upward curvature and the jump of $\Delta C/T$ increased.[19] Change in γ_n can be resolved but is small, within 10%. Therefore, the effects of the molecule intercalation and reducing carrier density are qualitatively similar to each other. To perform a similar quantitative analysis on the molecule-intercalated compounds, we fitted these data to the empirical theory[27] with an assumption of an isotopically gapped state. The results reproduced the experimental data quite well (not shown), and then, we obtained γ_n and $2\Delta_0/k_BT_c$ values. We will discuss their d dependence in the next section.

In Fig. 7, the field dependence of the electronic specific heat obtained from Fig. 5, is plotted as $\gamma(H) \equiv [\Delta C(H) - \Delta C(0)]/T$ normalized by γ_n, $\gamma(H)/\gamma_n$, as a function of the normalized field, H/H_{c2}. The field dependence of $\gamma(H)$ is known as a powerful tool for investigating the low-energy quasiparticle state.[28] In superconductors having substantial anisotropy or nodal structure in the superconducting gap, the quasiparticle spectrum is Doppler shifted by the magnetic field, leading to a finite density of states at the Fermi energy. This Doppler effect leads to a steeper increase in the specific heat at low fields and low temperatures than the H-linear behavior expected in fully gapped superconductors. In Li-intercalated compounds, it has been found that $\gamma(H)/\gamma_n$ evolves much steeper than H-linear behavior, as is clearly seen in Fig. 6,[17] but H-linear behavior has been observed at the lowest doping with $x \sim 0.05$.[19] $\gamma(H)/\gamma_n$ in molecule-intercalated compounds is close to that in $\mathrm{Li}_{0.12}\mathrm{ZrNCl}$, implying that the superconducting gap is kept highly anisotropic after molecule intercalation, at least at the

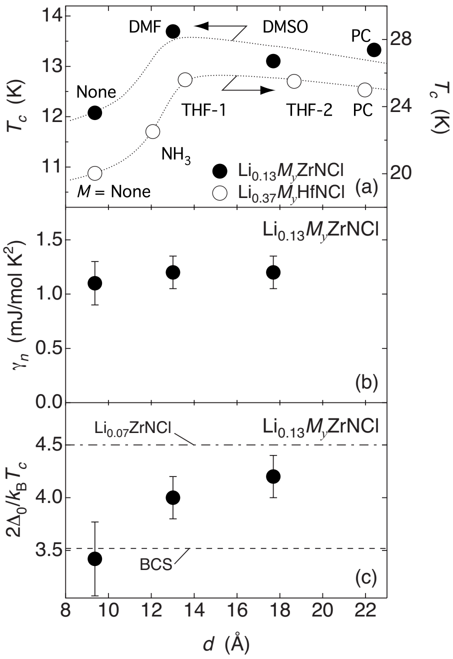

FIG. 8. Interlayer spacing d dependence of (a) T_c, (b) electronic specific-heat coefficient γ_n, and (c) superconducting gap ratio $2\Delta_0/k_BT_c$ in Li_xM_yZrNCl with $x=0.13$. In (a), T_c in Li_xM_yHfNCl is also shown (Ref. 18). Data points of M=PC in Zr compounds are taken from Ref. 23. Dotted lines are guide for the eyes. In (c), the dashed-dotted line indicates $2\Delta_0/k_BT_c$ value obtained in $Li_{0.07}ZrNCl$. The dashed line represents the BCS weak-coupling limit, $2\Delta_0/k_BT_c=3.52$.

same doping region. The anisotropic gap state has also been supported by recent muon spin rotation measurements.[20]

IV. DISCUSSIONS

Based on the above experimental observations, we will summarize the effects of organic molecule intercalation. In Figs. 8(a)–8(c), T_c, γ_n, and $2\Delta_0/k_BT_c$ are plotted as a function of interlayer spacing d. d dependence of T_c in Hf analog ($Li_{0.37}M_yHfNCl$), taken from Ref. 18, is also shown in Fig. 8(a). With increasing d, T_c initially increases steeply but becomes nearly insensitive to d and rather shows a slight decrease with further increase in $d \gtrsim 14$ Å. As clearly seen in Fig. 8(a), d dependence of T_c in Zr compounds is qualitatively similar to that in Hf compounds. γ_n was found to be almost constant at $\gamma_n \sim 1.1$ mJ/mol K^2, with respect to d. In contrast, $2\Delta_0/k_BT_c$ is apparently enhanced by molecule intercalation and considerably exceeds the weak-coupling value of $2\Delta_0/k_BT_c=3.54$. These results strongly indicate that T_c enhancement through molecule intercalation is attributed to reinforcement of the pairing interaction rather than the DOS at the Fermi level.

The effect of organic molecule intercalation on T_c has been comprehensively studied in misfit-layer sulfides.[29] In sulfides TaS_2 and NbS_2, where superconductivity appears even in pristine compounds with $T_c=0.8$ K and 6 K, respectively, specific-heat measurements have been reported so far.[30,31] Upon molecule intercalation, T_c is enhanced (reduced) in TaS_2 (NbS_2) but becomes a constant value ($\sim$4 K) with further enlargement of d. It has been revealed that γ_n, and the size of the specific-heat jump at T_c are enhanced (reduced) upon the intercalation concomitantly with T_c in TaS_2 (NbS_2), indicating that both the DOS at the Fermi level and electron-phonon coupling strength are responsible for the T_c change observed. It should be noted that, as mentioned in Sec. II, no discernible change was found in the Raman spectra after molecule cointercalation with Li, indicating that intercalation does not affect the lattice vibration in Li_xZrNCl and the vibration of the molecules themselves can be negligible. Therefore, the effect of two dimensionality is found to be significantly different from sulfide superconductors, suggesting that a distinct mechanism governs the T_c in the layered nitrides.

According to the interlayer-coupling theory, which has been discussed in terms of the high-T_c superconductivity in cuprates,[32,33] T_c is expected to be proportional to the interlayer-coupling strength, that is, inversely proportional to the interlayer separation, $T_c \propto 1/d$. Apparently, it would be valid neither in cuprates[34] nor in the present materials because of T_c enhancement from enlarging d. However, the slight decrease in T_c observed at $d \gtrsim 14$ Å may be attributed to the reduction in the interlayer coupling.

A concomitant evolution of the pairing interaction and T_c has also been seen when reducing the carrier density. In Li_xZrNCl, by reducing doping from $x=0.12$ to 0.07, T_c is enhanced from 12.5 K to the maximum value of 15.2 K [see, Fig. 1(b)], and $2\Delta_0/k_BT_c$ evolves from the nearly BCS value to $2\Delta_0/k_BT_c=4.5$, which is also the maximum among the values obtained from the specific heat.[19] As shown in Fig. 8(c), even in molecule intercalation, $2\Delta_0/k_BT_c$ approaches to a maximum value with T_c. Therefore, it would be natural to consider that the evolution of the pairing interaction from reduced doping and enlarging interlayer spacing are attributed to the same mechanism. A recent study of the doping variation in the magnetic susceptibility along with theoretical calculations[19,35] have suggested an evolution of magnetic fluctuations from reduced carrier density and its contribution to the pairing interaction in the parent material. According to the theory, in Li_xZrNCl which has two degenerated nearly cylindrical Fermi surfaces centered at K and K' points in the hexagonal Brillouin zone, the pairing can be mediated by a spin fluctuation,[21] and the enhancement and the subsequent constant behavior of T_c with improvement of two dimensionality have been demonstrated by the calculation.[35] Within this scheme, as the interlayer spacing d is increased, the Fermi surface warping along the k_z direction must be reduced due to enhanced two dimensionality and that would result in an increase in nesting of the Fermi surface. This improved nesting would enhance the spin fluctuation, which would in turn reinforce the superconducting pairing interaction among electrons. This scenario is in perfect consistency with the present result, which unambiguously reveals that the pairing interaction is increased by enhanced two dimensionality.

V. SUMMARY

We have investigated the effect of two dimensionality on superconductivity in Li_xM_yZrNCl with cointercalated organic molecules M with Li, by the specific-heat measurements. A concomitant enhancement of the superconducting coupling strength in parallel with T_c has been observed upon the enlargement of the interlayer distance whereas the density of states at the Fermi level was kept at an almost constant value, indicating that the reinforcement of the pairing interaction is responsible for the enhancement of T_c as was observed with the reduction in carrier density in Li_xZrNCl. The present results do not contradict the recent prediction of spin fluctuation mediated pairing, which has been argued experimentally and theoretically.

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