Two dimensional nature of superconductivity in intercalated layered systems \( \text{Li}_x \text{HfNCl} \) and \( \text{Li}_x \text{ZrNCl} \): muon spin relaxation and magnetization measurements

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Abstract

We report muon spin relaxation (\( \mu \)SR) and magnetization measurements, together with synthesis and characterization, of the Li-intercalated layered superconductors \( \text{Li}_x \text{HfNCl} \) and \( \text{Li}_x \text{ZrNCl} \) with/without co-intercalation of THF
(tetrahydrofuran) or PC (propylene carbonate). The 3-dimensional (3-d) superfluid density \( n_s/m^* \) (superconducting carrier density / effective mass), as well as the two dimensional superfluid density \( n_{s2d}/m_{ab}^* \) (2-dimensional (2-d) area density of superconducting carriers / ab-plane effective mass), have been derived from the \( \mu \)SR results of the magnetic-field penetration depth \( \lambda_{ab} \) observed with external magnetic field applied perpendicular to the 2-d honeycomb layer of HfN / ZrN. In a plot of \( T_c \) versus \( n_{s2d}/m_{ab}^* \), most of the results lie close to the linear relationship found for underdoped high-\( T_c \) cuprate (HTSC) and layered organic BEDT superconductors. In Li\(_x\)ZrNCl without THF intercalation, the superfluid density and \( T_c \) for \( x = 0.17 \) and 0.4 do not show much difference, reminiscent of \( \mu \)SR results for some overdoped HTSC systems. Together with the absence of dependence of \( T_c \) on average interlayer distance among ZrN / HfN layers, these results suggest that the 2-d superfluid density \( n_{s2d}/m_{ab}^* \) is a dominant determining factor for \( T_c \) in the intercalated nitride-chloride systems. We also report \( \mu \)SR and magnetization results on depinning of flux vortices, and the magnetization results for the upper critical field \( H_{c2} \) and the penetration depth \( \lambda \). Reasonable agreement was obtained between \( \mu \)SR and magnetization estimates of \( \lambda \). We discuss the two dimensional nature of superconductivity in the nitride-chloride systems based on these results.

78.30.Hv, 78.40.Ha, 72.80.Ga, 75.45.+j
Layered superconductors, such as high-$T_c$ cuprates (HTSC) or organic BEDT systems, have been a subject of extensive research effort for decades. These systems show rich novel phenomena, including superconducting fluctuations, pancake vortex, complicated vortex phase diagrams, and interlayer Josephson effects. High-$T_c$ cuprate superconductors have been investigated extensively as prototypical layered superconductors. The cuprates have a merit that their carrier concentration can be controlled by chemical substitutions and/or oxygen contents. On the other hand, it has not been easy to control the interlayer distance in cuprates. In general, superconductivity of these layered systems is deeply related to in-plane features as well as interlayer couplings. For overall understanding of superconductivity in these systems, it would be essential to elucidate interplay between in-plane and interplane properties. Despite extensive research effort, however, detailed roles of dimensionality are yet to be clarified in these systems.

Recently, superconductivity was discovered in ZrNCl and HfNCl intercalated with alkali atoms (Li, Na, K) [1,2]. Systems based on ZrNCl have superconducting transition temperatures $T_c \leq 15$ K, while those based on HfNCl have $T_c \leq 25.5$ K. These systems can be co-intercalated with organic molecules, such as THF (tetrahydrofuran) or PC (propylene carbonate). The parent compounds ZrNCl and HfNCl are insulators which have a layered structure as shown in Fig. 1(a). Zr(Hf)-N honeycomb double layers are sandwiched by Cl layers, and a composite Cl-(ZrN)-(ZrN)-Cl layers form a stacking unit. Adjacent stacking units are bonded by weak van der Waals force. Alkali metal atoms and polar organic molecules such as THF or PC can be co-intercalated into the van der Waals gap of the parent compounds as shown schematically in Fig. 1(b). Intercalated alkali metal atoms are supposed to release electrons into Zr(Hf)-N double layers, which makes the system metallic and superconducting. On the other hand, intercalated organic molecules expand interlayer distance without changing Zr(Hf)-N honeycomb double layers. So we can control two separate parameters, carrier concentration and the stacking unit distance, in a single series of
nitride chlorides with the common superconducting slab. This unique feature could allow studies of layered superconductors from a new angle.

In this paper, we will present synthesis and characterization of a series of intercalated ZrNCl and HfNCl samples, together with studies of their superconducting properties using muon spin relaxation (µSR), magnetization, and resistivity measurements. A part of this work was presented in a conference [3], where we reported µSR results in HfNCl-Li$_{0.5}$-THF$_{0.3}$, showed that $T_c$ and the 2-d superfluid density in this system follow the correlations found in cuprates and BEDT systems, and discussed that this feature likely comes from departure from BCS condensation, which can be understood in terms of crossover from Bose-Einstein to BCS condensation. Subsequently, Tou et al. [4] reported an NMR Knight shift study which inferred a rather small density of states at the Fermi level in HfNCl-Li-THF, and discussed difficulty in explaining the high transition temperature $T_c$ in terms of the conventional BCS theory. Tou et al. [5] also reported a rather high upper critical field $H_{c2}(T \rightarrow 0) \sim 100$ kG, for the field applied perpendicular to the conducting planes, from magnetization and NMR measurements.

Extensive µSR measurements of the magnetic field penetration depth $\lambda$ have been performed to date in various superconducting systems, such as high-$T_c$ cuprates (HTSC) [6–13], fullerides [14,15], and two-dimensional (2-d) organic BEDT systems [16]. Universal nearly linear correlations have been found between $T_c$ and the muon spin relaxation rate $\sigma(T \rightarrow 0) \propto 1/\lambda^2 \propto n_s/m^*$ (superconducting carrier density / effective mass) in the underdoped region of many HTSC systems and in some other exotic superconductors [6,7] Such correlations are seen also in HTSC superconductors having extra perturbations, such as overdoping [8,12,17], (Cu,Zn) substitutions [18], or spontaneous formation of nano-scale regions with static stripe spin correlations [19,20]. In all these systems, $T_c$ follows the correlations with superfluid density found for less perturbed standard HTSC systems. These results indicate that the superfluid density is a determining factor for $T_c$ in the cuprates [21].

In general, a strong dependence of $T_c$ on the carrier density is not expected in conventional BCS theory [22] where $T_c$ is determined by the mediating boson (phonon) energy
scale and the density of states of carriers at the Fermi level which govern the charge-boson (electron-phonon) coupling. For 2-d metals, the density of states does not depend on the carrier density in the simplest case of non-interacting fermion gas. Therefore, the BCS theory has a fundamental difficulty in explaining the observed correlations. In contrast, an explicit dependence of $T_c$ can be expected for the condensation temperature $T_B$ in Bose-Einstein (BE) condensation of a simple Bose gas, as well as for the Kosterlitz-Thouless transition temperature $T_{KT}$ for a 2-d superfluid [23]. In BE and KT transitions, the transition temperature is determined simply by the number density and the mass, since the condensation is decoupled from the formation of condensing bosons in these two cases. The universality of the $T_c$ vs $n_s/m^*$ relationship observed beyond the difference of systems, such as cuprates, fullerides, orangics, etc., may be related to this feature. Pictures proposed to explain the correlations between $T_c$ and the superfluid density in the cuprates include crossover from Bose-Einstein to BCS condensation [24–28] and phase fluctuations [29]. In the present work, we extend our study to intercalated nitride-chloride systems, seeking further insights into such phenomenology.

We have also determined the upper critical field $H_{c2}$ of nitride-chloride systems from magnetization and resistivity measurements. Although it is not easy to determine $H_{c2}$ in layered superconductors due to the strong superconducting fluctuations, Hao et al. [30] developed an approach to overcome such difficulty using a model for reversible diamagnetic magnetization of type-II superconductors which have high $\kappa$ values. Here, $\kappa$ is the Ginzburg-Landau parameter defined as the ratio of the penetration depth $\lambda$ to the coherence length $\xi$. In this model, one calculates the free energy including the supercurrent kinetic energy, the magnetic-field energy, as well as the kinetic-energy and condensation-energy terms arising from suppression of the order parameter in the vortex core. This method has been successfully applied to various high-$T_c$ cuprate superconductors. We will apply this model to superconducting Hf(Zr)NCl in the temperature and field region where the effect of superconducting fluctuations is negligible.
II. SYNTHESIS AND CHARACTERIZATION

The parent compounds HfNCl and ZrNCl were synthesized by the reaction of Zr or Hf powder with vaporized NH₄Cl at 600 °C for 30 minutes in N₂ flow [31]. The resulting powder was sealed in a quartz ampule and was purified by a chemical vapor transport method with temperature gradient [32]. For the purification, an end of the ampule with pre-reacted powder was kept at 800 °C and the other end, where purified powder is collected, at 900 °C for three days. No impurity phase was detected in the purified powder from x-ray diffraction.

Since a Li-intercalated sample is sensitive to air, intercalation was performed in a glove box. We used three intercalation methods [33] to prepare a variety of samples: (i) Li-intercalated ZrNCl samples were prepared by soaking parent ZrNCl powder in three kinds of butyllithium solution. We used 2.0 M (mol/l) n-butyllithium solution in cyclohexane, 1.3 M sec-butyllithium solution in cyclohexane, and 1.7 M tert-butyllithium solution in pentane for this purpose. In this order, reducing ability becomes stronger and therefore higher concentration of Li atoms can be intercalated into the parent compound. We used solution which contained butyllithium corresponding to more than 2, 5, and 5 equivalents of ZrNCl for n-, sec-, and tert-butyllithium, to avoid the dilution of butyllithium in the intercalation process. (ii) We performed co-intercalation of Li and organic molecules into ZrNCl by soaking Li intercalated ZrNCl powder (prepared by the method (i) using n-Butyllithium solution) in enough THF or PC. (iii) Li- and THF-co-intercalated HfNCl samples were prepared by soaking HfNCl powder in various concentrations (2.5-100 mM) of lithium naphthalene (Li-naph) solution in THF. Since phase separation was often observed in the samples prepared by the method (iii), we selected single phase samples for the measurements in this study via characterization from $T_c$ as well as c-axis lattice constant. The Li- and THF-co-intercalated HfNCl sample with the largest c-axis lattice constant according to the method (iii) was prepared at Hiroshima University, while all the other samples at Columbia University. Table 1 shows a list of these samples.

The chemical composition was determined by inductively coupled plasma atomic emission
spectroscopy (ICP-AEM) and CHN elemental analysis. The powder samples were pressed into pellets under uniaxial stress and sealed in cells made of Kapton film and epoxy glue for x-ray measurements. The x-ray rocking curve of (00l) peaks for cleaved surface (inside of a pellet) shows a peak with half width at half maximum of \( \sim 8 \) degrees, which indicates that the bulk of the samples have well-aligned preferred orientation and are suitable for studies of anisotropic properties. Essentially similar rocking curves were also observed for as-prepared surfaces of pellets.

The superconducting transition temperature of the samples was determined from measurements of magnetic susceptibility \( \chi \). In Fig. 2, we show the results of \( \chi \) in intercalated ZrNCl specimens which were examined by \( \mu \)SR measurements. The values of \( \chi = M/H \) are of the order for ideal perfect diamagnetism \( -3/8\pi \) for spherical samples and \( -1/4\pi \) for long cylindrical samples with the field parallel to the cylinder axis. The determination of the absolute values of \( \chi \), however, can be affected by such factors as non-spherical sample shape, sample morphology and residual field in a SQUID magnetometer. These factors might have caused deviation of some of the zero-field cooled shielding values of \( \chi \) from \( -1/4\pi \).

In Table 1, we summarize the composition, synthesis method, distance between adjacent stacking units (1/3 of the c-axis lattice constant \( c_0 \), see Fig. 1), and the superconducting transition temperature \( T_c \) for these samples. The stacking unit distance is 9.4 Å for the Li-intercalated samples prepared by the method (i) without co-intercalation of organic molecules. This value is almost the same as that for unintercalated parent compound (9.3 Å) without Li. With increasing Li concentration \( x \) from 0.17 to 0.6 (in the samples without co-intercalation of organic molecules), \( T_c \) decreases from 14.2 K to 11.7 K. Figure 3(a) shows the \( x \) dependence of \( T_c \) in \( \text{Li}_x\text{ZrNCl} \) and \( \text{Li}_x\text{HfNCl} \) samples, with/without co-intercalation, obtained in the present study. In Fig. 3 and Table 1, we find that: (1) \( T_c \) shows a slow reduction with increasing \( x \); (2) for close \( x \) values, \( T_c \) does not depend much on the stacking-unit distance \( c_0/3 \) (see Fig. 3(b)). These results are qualitatively consistent with the reported results in the Li, K, and Na doped ZrNCl samples with/without co-intercalation of organic molecules [34]. Decrease of \( T_c \) with increasing charge doping is reminiscent of the case of
overdoped high-$T_c$ cuprate superconductors.

To the best of our knowledge, this is the first report of success in Li-THF intercalation into ZrNCl by sec- and tert-butyllithium. The stacking unit thickness is 13.3 or 18.7 Å for the methods (ii) and (iii). As has been reported, $T_c$ is almost unaffected by the expansion of the stacking-unit distance from $\sim 9.4$ Å to $\sim 13.3$ Å for the samples with Li content $x \sim 0.17$ (see Fig. 2 (b)). Systems based on HfNCl has $T_c = 25.5$ K, nearly a factor of two higher than that for intercalated ZrNCl.

III. $\mu$SR: EXPERIMENTAL

Our $\mu$SR experiments were performed at TRIUMF, the Canadian National Accelerator Laboratory located in Vancouver, Canada, which provided a high intensity and polarized beam of positive muons. Each pressed pellet sample, with the c-axis aligned, was sealed in a sample cell which has a Kapton window and mounted in a He gas-flow cryostat with the c-axis parallel to the direction of muon beam. Transverse external field (TF) was applied parallel to the beam direction, while muons are injected with their initial spin polarization perpendicular to the field/beam direction. Low-momentum (surface) muons with the incident momentum of 29.8 MeV/c were implanted in the pellet specimens. The average stopping depth, 100-200 mg/cm$^2$, assured that the majority of muons are stopped within the specimen, after going through Kapton windows of the cryostat and the sample cell.

Plastic scintillation counters were used to detect the arrival of a positive muon and its decay into a positron, and the decay-event histogram was obtained, as a function of muon residence time $t$ which corresponds to the time difference of the muon arrival and positron decay signals. The time evolution of muon spin direction/polarization was obtained from the angular asymmetry of positron histograms, after correction for the exponential decay $\exp(-t/\tau_\mu)$, where $\tau_\mu = 2.2$ μs is the mean lifetime of a positive muon. Details of $\mu$SR technique can be found, for example, in refs [35–37].
The asymmetry time spectra $A(t)$ were fit to a functional form:

$$A(t) = A(0) \exp(-\sigma^2 t^2/2) \times \cos(\omega t + \phi),$$

where $A(0)$ is the initial decay asymmetry at $t = 0$. The muon spin precesses at the frequencies $\omega = \gamma_\mu H_{ext}$, where $\gamma_\mu$ is the gyromagnetic ratio of a muon ($2\pi \times 13.554$ MHz/kG) and $H_{ext}$ denotes the transverse external magnetic field. As shown in Fig. 4, for an example of Li$_{0.17}$ZrNCl, this oscillation exhibits faster damping in the superconducting state due to inhomogeneous distribution of internal magnetic fields in the flux vortex structure. In pressed pellet samples of random or oriented powder, this relaxation can usually be approximated by a Gaussian decay which defines the muon spin relaxation rate $\sigma$.

For systems except for ZrNCl-Li-THF, the $\mu$SR results were analysed by assuming a single-component signal, which shows a reasonable agreement to the data as in Fig. 4(b). In ZrNCl co-intercalated with Li and THF, the relative value of the shielding susceptibility was significantly lower than those of other samples, as shown in Fig. 2. Although it is not clear, this reduced susceptibility could possibly imply a finite fraction of superconducting volume. As a precautionary measure, by fitting selected low-temperature signals in field-cooled and zero-field cooled procedures to an asymmetry function having two-component signals, we estimated an upper-limit of the relaxation rate for the superconducting fraction. This upper-limit is shown (in Figs. 6 and 7) by the error-bar placed to the right side of the main point for $\sigma$ which was obtained for a single-component asymmetry function.

**IV. $\mu$SR: SPECTRA AND RELAXATION RATE**

Figure 4 shows time spectra of muon decay asymmetry for a representative sample above and below $T_c$. In the normal state above $T_c$, the oscillation shows a small relaxation due to nuclear dipole fields. We denote this relaxation rate as $\sigma_n$. Below $T_c$, the relaxation becomes faster due to additional field distribution from the flux vortex lattice. For each specimen, the zero-field $\mu$SR spectra obtained above and well below $T_c$ did not show any
difference. This assures that the temperature dependence of the relaxation rate observed in TF is due to superconductivity alone, and also implies that there is no detectable effect of time-reversal symmetry breaking, contrary to the case of UPt₃ [38] and Sr₂RuO₄ [39].

The effect of the superconducting vortex lattice can be obtained by subtracting this normal-state background $\sigma_n$ from the observed relaxation rate $\sigma_{ob}$. Since the nuclear dipolar broadening and superconducting broadening of the internal fields do not add coherently, here we adopt quadratic subtraction to obtain the relaxation rate $\sigma$ due to superconductivity as:

$$\sigma = \sqrt{\sigma_{ob}^2 - \sigma_n^2} \quad for \quad (\sigma_{ob} \geq \sigma_n)$$

and

$$\sigma = -\sqrt{\sigma_n^2 - \sigma_{ob}^2} \quad for \quad (\sigma_{ob} < \sigma_n).$$

Note that this procedure makes the error bar rather large around $\sigma = 0$.

Figure 5(a) shows the temperature dependence of the relaxation rate $\sigma$ for the samples co-intercalated with organic molecules having expanded interlayer distance. With decreasing temperature, the relaxation rate begins to increase below the superconducting transition temperature $T_c$. At the flux-pinning temperature $T_p$, the zero-field-cooling (ZFC) curve begins to deviate from the field-cooling (FC) curve. In the ZFC procedures, flux vortices are required to enter the specimen from its edge and move a large distance before reaching their equilibrium position. Below the pinning temperature $T_p$, this long-distance flux motion could be prevented by the flux pinning, resulting in an highly inequilibrium flux lattice and more inhomogeneous field distribution at muon sites. This behavior has been observed in earlier $\mu$SR studies of HTSC [40], BEDT [16] and some other systems. In both systems shown in Fig. 5(a), we find that $T_p$ is much lower than $T_c$, which is a characteristic feature for highly 2-d superconductors. The $\mu$SR results of $T_p$ for the present systems agree well with those from magnetization measurements discussed in Section VII.

We performed FC measurements using a wide range of external transverse magnetic fields $H_{ext}$, and found no significant dependence of $\sigma$ on $H_{ext}$ from 40 G to 1000 G, as shown in Fig. 5. In TF-$\mu$SR measurements in highly 2-d superconductors, such as Bi2212
or (BEDT-TTF)$_2$Cu(NCS)$_2$, application of a high external magnetic field transforms 3-d flux vortex structure into 2-d pancake vortices, since higher field implies stronger coupling of flux vortices within a given plane and higher chance for the vortex location in each plane to be determined by random defect position on each plane [41]. The absence of field dependence in our measurements implies that corrections for the 2-d vortex effect is not necessary in the present study. This situation is expected for our c-axis aligned powder specimens. The relaxation rate $\sigma(T)$ shows a tendency of saturation at low temperatures in all of the measured samples of nitride-chloride systems in the present study. This behavior is characteristic for s-wave superconductors. However, experiments using high-quality single crystals are required for a conclusive determination of the superconducting pairing symmetry. In the case of HTSC cuprates, d-wave pairing was established only after $\mu$SR results on high-quality crystals of YBa$_2$Cu$_3$O$_y$ became available [42].

Figure 5(b) shows the temperature dependence of $\sigma$ for the samples without organic co-intercalant. The dependence of $\sigma$ on temperature $T$ and field $H_{ext}$ of the field-cooling results was essentially similar to that for specimens with co-intercalation in Fig. 5(a). In these systems, we determined the pinning temperature $T_p$ by magnetization measurements instead of by $\mu$SR, and show the results in section VII.

V. $\mu$SR: COMPARISON WITH OTHER SYSTEMS AND SUPERFLUID ENERGY SCALES

The $\mu$SR relaxation rate due to the penetration depth is related to the superconducting carrier density $n_s$, effective mass $m^*$, the coherence length $\xi$ and the mean free path $l$ as

$$\sigma \propto \lambda^{-2} = \frac{4 \pi e^2}{c^2} \times \frac{n_s}{m^*} \times \frac{1}{1 + \xi/l}.$$  

The proportionality to $n_s/m^*$ comes from the fact that this effect is caused by the superconducting screening current, and consequently reflecting the current density in a similar way to the normal state conductivity of a metal which is proportional to the carrier density divided by the effective mass. As will be shown later, $\xi$ is estimated to be 80-90 Å.
in the present nitride-chloride systems. The mean free path cannot be determined at the moment, since a high-quality single crystal is not yet available. In this situation, we proceed with the following arguments by assuming that the system falls in the clean limit ($\xi << l$). Clean limit has been confirmed in many other strongly type-II superconductors, such as the cuprates and BEDT systems.

In highly anisotropic 2-d superconductors, the penetration depth measured with the external field parallel and perpendicular to the conducting plane could be very different. For the geometry with $H_{ext}$ perpendicular to the conducting plane, related to the in-plane penetration depth $\lambda_{ab}$ as in the present study, the superconducting screening current flows within the plane, resulting in the more effective partial screening of $H_{ext}$ and the shorter $\lambda$ compared to the case with $H_{ext}$ parallel to the planes. In the present work, our specimen has a highly-oriented c-axis direction within +/- 8 degrees, and we regard our specimen as equivalent to single crystal specimens in terms of anisotropy. A theory/simulation work [43] shows that for un-oriented ceramic specimens of highly 2-d superconductors, value of $\sigma$ should be reduced by a factor of 1/1.4 from the value for single crystals observed with $H_{ext}$ applied perpendicular to the conducting planes.

In Fig. 6, in a plot of $T_c$ versus the low-temperature relaxation rate $\sigma(T \to 0) \propto n_s/m^*$, we compare the results of the present nitride-chloride systems with those from cuprate and organic BEDT superconductors. The point for the BEDT system was obtained in $\mu$SR measurements using single crystal specimens [16]. The shaded area denoted as cuprates represents the universal linear correlations found for un-oriented ceramic specimens of underdoped YBCO systems: we multiplied the relaxation rate in these YBCO by a factor of 1.4 to account for the difference between single crystal and un-oriented ceramic specimens. The data points lie in possibly two different groups having different slopes in the $T_c/\sigma$ relation. The first group with a higher slope includes the present nitride-chloride systems with co-intercalation of organic molecules and the BEDT system, all of which having highly 2-d character as demonstrated by their depinning temperature $T_p$ being nearly a 1/3 to 1/2 of $T_c$. The second group includes YBCO cuprates and nitride-chloride systems without organic
co-intercalation, all of which have more 3 dimensional (3-d) character in the flux pinning property with $T_p$ closer to $T_c$. The irreversibility and depinning behavior in Li$_x$ZrNCl without organic co-intercalation was studied not by $\mu$SR but by magnetization measurements as described in section VII.

The relaxation rate observed by $\mu$SR is determined by the 3-d superfluid density $n_s/m^*$, as this is a phenomenon caused by the screening supercurrent density in bulk specimens. With the knowledge of interlayer spacing $c_{int}$, one can convert 3-d density $n_s/m^*$ into 2-d density on each conducting plane as $n_{s2d}/m^* = n_s/m^* \times c_{int}$. For systems having double-layer conducting planes, such as the present nitride chlorides or some family of the cuprates, the average interlayer spacing depends on whether or not the double layer is regarded as a single conducting unit or two. In our previous reports for cuprates [26], we treated the double layer as two single layers. We shall follow this approach here, and define the $c_{int}$ to be a half of the stacking unit distance as $c_{int} = c_0/6$.

In Fig. 7, we show a plot of $T_c$ versus the 2-d superfluid density $n_{s2d}/m^*$ represented by the value $\sigma(T \to 0) \times c_{int}$. We include a point obtained in c-axis oriented ceramic specimen of YBa$_2$Cu$_3$O$_7$ [44] (without multiplying a factor 1.4 to $\sigma$ since this specimen had an almost perfect alignment of c-axis direction). We find that most of the data points share a unique slope in Fig. 7. This result suggests two features: (1) within the nitride-chloride systems, 2-d superfluid density $n_{s2d}/m^*$ is a determining factor for $T_c$; and (2) the 2-d superfluid density may even be a fundamental determining factor for $T_c$ among different superconducting systems. However, the second conclusion (2) must be taken with caution, because, this analysis depends on our treatment regarding single versus double layers, and also because recent data on Tl2201 [8] and Bi2201 [45] cuprates, having very large interlayer distance $c_{int} > 12$ Å, show universal behavior with the results from YBCO ($c_{int} \sim 6$ Å) only in a 3-d plot like Fig. 6 but not in a 2-d plot like Fig. 7 [26]. In contrast, the conclusion (1) is more robust, since all the nitride-chloride systems have double conducting layers, and since the predominant 2-d character is consistent with the absence of dependence of $T_c$ on interlayer spacing in nitride-chlorides shown in Fig. 3(b).
Since the Fermi energy of a 2-d metal is proportional to the 2-d carrier density $n_{2d}$ divided by the in-plane effective mass $m^*$, as $T_F = (\hbar^2 \pi) n_{2d}/m^*$, the horizontal axis of Fig. 7 can be converted into an energy scale representing superconducting condensate. This conversion from penetration depth to the superfluid energy scale was first attempted by Uemura et al. [7] in 1991 and later followed by other researchers, including Emery and Kivelson [29].

In order to do such a conversion, one needs to obtain absolute values of the penetration depth $\lambda$ from the relaxation rate $\sigma$. The numerical factor in this $\sigma$ to $\lambda$ conversion in $\sigma \propto \lambda^{-2}$ depends on models used for analyses of relaxation function line shapes, fitting range of data analyses, treatment of single crystal versus ceramic samples, and some other factors. The Gaussian decay, which fits most of the data from ceramic samples quite well, is significantly different from the ideal field distribution $P(H)$ expected for a perfect Abrikosov vortex lattice in triangular lattice. So, using a theoretical second moment for $P(H)$ in Abrikosov lattice is not necessarily appropriate for data analyses in real experiments. After various simulations and consistency checks, we decided to adopt a factor which gives $\lambda = 2,700 \text{ Å}$ for $\sigma = 1 \mu s^{-1}$ for a triangular lattice. Note that this conversion is for a standard triangular lattice, contrary to the statements of Tou and collaborators [4,5] who have erroneously cited that we calculated $\lambda$ for a square vortex lattice. Then we can derive $n_{s2d}/m^*$ from the observed values of $\sigma$ and known values of $c_{int}$. In the horizontal axis of Fig. 7, we attach the 2-d Fermi temperature $T_{F2d}$ corresponding to the 2-d superfluid density obtained in the above-mentioned procedure.

A 2-d superfluid of bose gas, such as thin films of liquid He, undergoes superfluid to normal transition via a thermal excitation of unbound flux vortices, as shown by Kosterlitz and Thouless (KT) [23]. For paired fermion systems composed of $n$ fermions with mass $m$, forming a superfluid with boson density $n/2$ and mass $2m$, the Kosterlitz-Thouless transition temperature $T_{KT}$ becomes 1/8 of the 2-d Fermi temperature $T_{F2d}$ of the corresponding fermion system. In the KT theory, the 2-d superfluid density at the transition temperature $T_{KT}$ should follow system-independent universal behavior: namely, $(\hbar^2 \pi) \times n_{s2d}/m^*$ at $T = T_{KT}$ equals $T_{F2d}/8$. This universal relation was first confirmed by an experiment on He thin films [46].
In systems close to ideal Bose-gas, the 2-d superfluid density shows almost no reduction between $T = 0$ and $T = T_{KT}$ [46]. Thus, in such a case, we would expect the points in Fig. 7 (based on $n_{s2d}/m^*(T = 0)$) to lie on the $T_{KT}$ line. In thin films of BCS superconductors, the superfluid density shows much reduction from the value of $T = 0$ to $T = T_{KT}$, and the “KT jump of superfluid density” becomes invisible. This corresponds to the situation where the points in Fig. 7 lie far in the right side of the $T_{KT}$ line. In Fig. 7, most of the points lie about a factor of 2 away from the $T_{KT}$ line. The linear relation between $T_c$ and $n_{s2d}/m^*(T = 0)$ suggests relevance to the KT transition, as pointed out by Emery and Kivelson [29]. However, the deviation from the $T_{KT}$ line implies serious difference from the ideal KT situation.

VI. MAGNETIZATION MEASUREMENTS: EXPERIMENTAL

Magnetization measurements were performed using a SQUID magnetometer (Quantum-Design) at Columbia. Aligned pressed samples were sealed in quartz ampules. The raw response curve was corrected by the subtraction of the quartz background curve measured in advance. In the normal state of the superconducting Hf(Zr)NCl samples, as well as the parent compounds, weak-ferromagnetic behavior is observed up to room temperature. This weak-ferromagnetic behavior changes by the intercalation. Therefore, we subtracted the weak-ferromagnetic contribution. We estimated this by extrapolating temperature dependence, assuming the Curie-Weiss law ($M = C/(T - \theta)$) and fitting the normal state magnetization in the temperature range of $2.5T_c \leq T \leq 5T_c$. In this temperature range, superconducting fluctuations can be neglected and the temperature dependence is slightly concave. We only used the data with the extrapolated weak-ferromagnetic contribution smaller than 10 % of the diamagnetic magnetization, to avoid an error from the assumption of the Curie-Weiss temperature dependence. The model developed by Hao et al. [30] was applied to the analysis of the reversible region. In this model, reduced (dimensionless) magnetization $M' = M/\sqrt{2}H_c(T)$ and field $H' = H/\sqrt{2}H_c(T)$ scales as a single function that contains the
Ginzburg-Landau parameter $\kappa$ as a unique parameter. In our analysis, we optimized $H_c(T)$, in addition to $\kappa$ as a parameter independent of temperature. Resistivity measurements were performed using a well-aligned pressed sample with four electrodes that is sealed in a cell made of Kapton film and epoxy glue.

VII. MAGNETIZATION MEASUREMENTS: SUPERCONDUCTING PROPERTIES

Magnetization measurements were performed in Li$_{0.17}$ZrNCl and Li$_{0.15}$THF$_{0.08}$ZrNCl with magnetic fields applied parallel to the c-axis. Figure 8 shows the results obtained after the corrections for the quartz sample background and for the weak-ferromagnetic contribution. We note that a crossing point exists in the $M(T)$ curve under various magnetic fields for each system, which is characteristic of quasi-two-dimensional superconductors [47]. There are reversible temperature regions where ZFC and FC magnetization curves overlap each other. Below a certain temperature (the pinning temperature $T_p$), ZFC and FC magnetization curves deviate. We notice that the reversible region is wider for Li$_{0.15}$THF$_{0.08}$ZrNCl. This result is consistent with a picture that, by the expansion of the interlayer distance, the interlayer coupling become weaker and the pinning of the vortices becomes less effective.

In the data analyses in the reversible region of Li$_{0.17}$ZrNCl and Li$_{0.15}$THF$_{0.08}$ZrNCl, we confined to the temperature region apart from $T_c(H)$ in order to avoid ambiguity due to the superconducting fluctuations. As shown in Fig. 9, the data scale quite well to Hao’s model in the whole reversible temperature range below $T_c$ for the both systems. For all the data, $M' << H'$ and hence the demagnetization factor can be ignored. This analysis yielded values of $\kappa$ ranging between 50 and 80 (see Table 1), which indicates that these compounds are extreme type-II superconductors. In Fig. 10, we show the values of the upper critical field $H_{c2,\parallel c}(T)$ obtained down to $T = 2$ K in this process using Hao’s model. The temperature dependence of $H_{c2,\parallel c}(T)$ fits well to an empirical formula $H_{c2,\parallel c}(0)[1-(T/T_c)^2]$, as shown by the dashed lines in Fig. 10. We emphasize that the low temperature limit value
\(H_{c2,//c}(T \to 0)\) can be obtained almost without any extrapolation using this formula: the resulting values are shown in Table 1. The \(H_{c2,//c}\) value of \(\sim 4-5\) T in ZrNCl-Li-THF system is about a factor of 2 smaller than \(H_{c2} \sim 10\) T in HfNCl-Li-THF system reported by Tou et al [5]. These results might indicate that \(H_{c2}\) roughly scales with \(T_c\). A similar nearly linear relation between \(H_{c2}\) and \(T_c\) can be found in the \(H_{c2}\) values for high-\(T_c\) cuprate superconductors in the optimum doping region.

The critical temperature \(T_c\) obtained using Hao’s model is 14.9 K for both samples, which agrees with the estimate from the onset of diamagnetism due to superconductivity. We notice that at \(H = 55\) kG above \(H_{c2,//c}(0)\), a diamagnetic behavior due to superconducting fluctuation was observed in magnetization as shown in Fig. 8. Similar results due to critical fluctuations have been reported in HTSC [48–50] and BEDT [51] systems. We obtained the in-plane coherence length \(\xi_{ab}(0)\) and the in-plane penetration depth \(\lambda_{ab,M}(0)\) using expressions \(H_{c2}(0) = \phi_0/2\pi\xi(0)^2\) and \(\kappa = \lambda/\xi\). These results are also summarized in Table 1. We note that \(H_{c2,//c}(0)\), and \(\xi_{ab}(0)\) are almost unaffected by the interlayer distance. This agrees with the view that the essence of the superconductivity in Hf(Zr)NCl is dominated in Hf(Zr)-N honeycomb double layers. The values of the penetration depth determined both from \(\mu\)SR and magnetization show reasonable agreement, although the former is \(\sim 20\%\) smaller than the latter for both compounds.

In magnetization measurements (see Fig. 8) and \(\mu\)SR measurements (see Fig. 5(a)), the results become history dependent below a pinning temperature \(T_p\) for a given external field \(H_{ext}\). This feature can be expressed by defining the irreversibility field \(H_{irr}\) for a given temperature \(T\) as \(H_{ext}(T = T_p) = H_{irr}\). Figure 10 also includes \(H_{irr}\) as a function of temperature, determined from magnetization and \(\mu\)SR measurements. The results obtained from the two different techniques exhibit excellent agreement. ZrNCl superconductors have a quite large reversible region in the \(H-T\) plane. The temperature dependence of the irreversibility field fits well to a functional form \(H_{irr}(T) = H_{irr}(0)(T_c/T - 1)^n\), obtained for three-dimensionally fluctuating vortices [52], with \(n = 1.5\) at low fields below \(H \sim 0.4\) Tesla. This provides support to our assumption of 3-d vortex lines which we adopted in our anal-
yses of TF-μSR spectra taken below $H = 0.1$ Tesla. At higher fields, the fitting becomes worse, similarly to Ref. [52]. This may be related to a dimensional crossover from 3- to 2-d vortex fluctuations. More careful measurements are necessary to conclude this point.

In order to provide a cross-check for the results of $H_{c2}(T)$, we performed magnetoresistance measurements on Li$_{0.17}$ZrNCl. The temperature dependence of resistivity for two sets of field and current configurations is shown in Fig. 11. High resistivity of the order of 100 $m\Omega cm$ and negative slope of the resistivity in the normal state at low temperatures could be due to grain boundaries and may not be intrinsic. The observed superconducting transition is broadened by superconducting fluctuations, weakly superconducting regions such as grain boundaries, and by vortex motion due to Lorenz force. We notice that the resistive broadening is slightly larger for $H//c$, which is a natural consequence of significant superconducting fluctuations only for $H//c$. We defined $T_c(H)$ where resistivity shows 50 % drop of the maximum value. Figure 12 shows $H_{c2}(T)$ obtained in this procedure. These absolute values of $H_{c2}(0)$ for $H//c$ agree reasonably well with those from magnetization measurements, in spite of the unreliable definition due to the broad resistive transition. The difference between the temperature dependences of the magnetization (Fig. 10) and resistive (Fig. 12) $H_{c2}$ data may be due the above-mentioned limitations of the resistive measurements. The anisotropy ratio of the upper critical field $H_{c2,\perp c}/H_{c2,//c}$ is roughly 3 as shown in Fig. 12. Although we do not have data for the system with co-intercalation of THF or PC, the anisotropy ratio would presumably increase in more 2-d systems with larger stacking unit distance.

VIII. DISCUSSIONS AND CONCLUSIONS

The quasi-two-dimensional nature of the superconducting state appears in various superconducting properties of intercalated Hf(Zr)NCl. $T_c$ correlates with a 2-d superconducting carrier density $n_{s2d}$ divided by effective mass $m^*$ rather than the 3-d counterpart. Diamagnetic magnetization due to superconducting fluctuation for $H//c$ is observed at high temperatures and high fields. The crossing point exists in $M(T)$ curves measured at various
fields. The reversible region of magnetization becomes larger with the increase of interlayer distance, suggesting weaker interlayer coupling.

In addition to these results, we note that $T_c$, $n_{s2d}/m^*$, and $\xi_{ab}(H_{c2,\perp c})$, all show moderate dependence on chemical doping level which presumably represents the in-plane normal-state carrier concentration, while remaining almost independent of the stacking unit distance. These parameters are closely related to the superconductivity mechanism of this layered superconductor. Since the coherence length is a measure for the pair size, independence of $\xi_{ab}$ on interlayer distance implies that interlayer coupling does not affect the pair formation. It is then possible to consider a picture in which fluctuating superconductivity exists within a given layer, while the layers are coupled weakly by Josephson coupling to achieve 3-d bulk superconductivity.

On the other hand, $\lambda_{ab}$ and $T_p$ are strongly affected by the interlayer distance. The reduction of $\lambda_{ab}$ with increasing stacking-unit distance can be understood as a simple reduction of the supercurrent density caused by lower density of the planes. The strong dependence of $T_p$ on $c_{int}$ is not surprising: this behavior has been seen in many HTSC cuprates.

Our results show that Hf(Zr)NCl with variable interlayer distance as well as carrier concentration is suitable for systematic studies of layered superconductors. In addition, low $H_{c2}$ value of this compound makes it easier to cover the whole superconducting region in the $H$-$T$ plane, and helps our study of vortex phase diagram.

In Fig. 6 and Fig. 7, we have compared the results from the nitride-chlorides with other layered superconductors. All the arguments in the previous paragraphs, as well as Fig. 7, give an impression that 2-d properties are predominantly important factor of all of these layered superconductors. However, comparison among different cuprate systems having different interlayer spacing $c_{int}$ indicates that the 3-d interlayer coupling plays a very important role in determining $T_c$ in the cuprates. Furthermore, the observed results in Fig. 7 show about a factor 2 deviation from the $T_{KT}$ line. These results indicate that a simple theory for KT transition, whose $T_c = T_{KT}$ is unrelated to the interlayer coupling, is not applicable either to the cuprates nor to the nitride-chloride systems. Further experimental
and theoretical studies are required to determine the origin of this deviation. Studies of crossover from Bose Einstein to BCS condensation, in the case of 2-d systems, might provide a clue for understanding this feature.

The absolute values of the penetration depth $\lambda$, obtained from the $\mu$SR and magnetization measurements, show a reasonable agreement. We notice, however, about 20-30 % difference in the values from the two different methods (see Table 1). $\mu$SR and magnetization estimates of $\lambda$ often exhibit some disagreement of this magnitude, as can be found also in the cases of HTSC and organic systems. Ambiguity of $\lambda$ with 20-30 % would, however, correspond to $\sim 50 \%$ ambiguity in the estimate of the superfluid density. In this situation, it would be ideal if there were a method to cross-check the superfluid density derived from $\mu$SR results in a completely different perspective.

In Bi2212 cuprate systems, Corson et al. [53] measured the frequency dependent superfluid response, and found temperature $T_{KT}$ above which the superfluid density depends on the measuring frequency. The superfluid density observed at $T = T_{KT}$ was consistent with the value expected in the universal argument of KT. This provides an excellent system-independent calibration to the superfluid density. The difference between the superfluid density at $T_{KT}$ and at $T \to 0$ should correspond to the distance (in the horizontal direction) of the corresponding data point in Fig. 7 from the $T_{KT}$ line. The $\mu$SR Bi2212 data point in a plot like Fig. 7 lie about a factor 2-3 away from the $T_{KT}$ line. This factor agrees reasonably well with the reduction of the superfluid density from the $T = 0$ value to the $T = T_{KT}$ value observed by Corson et al. [53] in Bi2212 system in a similar doping region. This satisfactory cross-check for the Bi2212 system indicates that our choice of the conversion factor between $\sigma$ and $\lambda$ was reasonable, and the superfluid density derived by $\mu$SR is very reliable. Of course, comparisons among $\mu$SR data for different systems in a relative scale can be performed without being affected by an ambiguity of their absolute values of the superfluid density.

We performed $\mu$SR measurements on three different specimens based on ZrNCl with Li concentrations 0.15, 0.17 and 0.4, and found that the results of 2-d superfluid density $n_{s2d}/m^*$
for these systems do not show much difference among one another. This phenomenon could
be explained by two different possibilities: (a) not all the Li atoms donate carriers on
the ZrN planes, and the Li concentration $x$ does not serve as an indicator of normal-state
carrier concentration; or (b) all the Li atoms donate electrons to the ZrN planes, but only
a finite fraction of those normal-state carriers participate in the superfluid. The situation
(b) is similar to the case of overdoped HTSC cuprates [21,54], where an energy-balance in
the condensation process seems to determine the superfluid density. Further experiments
on normal-state transport properties are required to distinguish between (a) and (b) in the
nitride-chloride systems.

In conclusion, we have synthesized and characterized several different specimens of in-
tercalated nitride-chloride superconductors, and performed $\mu$SR and magnetization mea-
surements. The superconducting transition temperature $T_c$ and the upper critical field
$H_{c2,\perp}$ exhibit a nearly linear relation with the 2-d superfluid density $n_{s2d}/m^*$, while show-
ing almost no dependence on the stacking unit distance. These features suggest a highly
two-dimensional nature of superconductivity in the nitride-chloride system.

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FIG. 1. Schematic figures of the crystal structure of Hf(Zr)NCl (a) without intercalation and (b) co-intercalated with Li and THF. The stacking unit thickness ($= c_0/3$, where $c_0$ is c-axis lattice constant) is also shown.
FIG. 2. Magnetic susceptibility $\chi$ vs. temperature measured in $H = 5$ Oe in the field-cooling (FC) and zero-field-cooling (ZFC) procedures in the specimens of intercalated ZrNCl which were used in the $\mu$SR measurements.
FIG. 3. Dependence of $T_c$, as determined from the susceptibility, on (a) Li concentration $x$, and on (b) stacking-unit-distance $c_0/3$ in Li$_x$ZrNCl and Li$_x$HfNCl with/without co-intercalation of THF or PC.
FIG. 4. The time spectra of muon asymmetry $A(t)$ measured in Li$_{0.17}$ZrNCl at (a) $T = 19$ K (above $T_c$) and (b) $T = 2.5$ K (well below $T_c$) under the transverse external field of 500 G. The apparent precession frequency in this graph is modified from the actual precession frequency by the use of a rotating reference frame. The solid lines show a fit to Gaussian decay envelope.
FIG. 5. Temperature dependence of the muon spin relaxation rate $\sigma(T)$ in (a) Hf(Zr)NCl co-intercalated with Li atoms and THF, and (b) Li$_x$ZrNCl without co-intercalation. The upper panel (a) shows the results obtained in the field cooling (FC) and zero field cooling (ZFC) procedures, while the results in the lower panel (b) were obtained in the FC procedure. Dashed lines are guides to the eyes.
FIG. 6. Correlations between $T_c$ and the muon spin relaxation rate $\sigma(T \to 0)$ of intercalated Hf(Zr)NCl (present work), high-$T_c$ cuprates [6] and (BEDT-TTF)$_2$-Cu(NCS)$_2$ [16]. The horizontal axis is proportional to the 3-dimensional superfluid density $n_s/m^*$ in the ground state. The results of $\sigma$ for the cuprates, obtained using un-oriented ceramic specimens, are multiplied by a factor $\sim 1.4$ for the comparison with those from nitride-chloride and BEDT systems obtained using single crystals and oriented ceramic specimens.
FIG. 7. Correlations between $T_c$ and $\sigma(T \to 0) \times c_{\text{int}}$ of intercalated Hf(Zr)NCl, organic BEDT [16] and YBa$_2$Cu$_3$O$_7$ (YBCO) [44], where $c_{\text{int}}$ stands for average interlayer distance. We regard the double layers in the nitride-chlorides and cuprates as two separate layers, and thus assume $c_{\text{int}} = c_0/6$ for the nitride chlorides and $c_{\text{int}} \sim 6\text{Å}$ for YBCO. The horizontal axis is proportional to the 2-d superfluid density $n_{s2d}/m^*$. To the horizontal axis, we also attach the corresponding energy scale, 2-dimensional Fermi temperature $T_{F2d}$, obtained from the 2-d superfluid density.
FIG. 8. Temperature dependence of the magnetization of (a) Li$_{0.17}$ZrNCl and (b) Li$_{0.15}$THF$_{0.08}$ZrNCl, in external magnetic fields applied parallel to the c axis. For the plotted data, the quartz ampule background is corrected and the weak-ferromagnetic contribution is subtracted.
FIG. 9. Magnetization as a function of applied field (parallel to the c-axis) in (a) Li$_{0.17}$ZrNCl and (b) Li$_{0.15}$THF$_{0.08}$ZrNCl, shown in the reduced (dimensionless) units. The solid curves represent a fit to the model of Hao et al. [30]
FIG. 10. Temperature dependence of the upper critical field $H_{c2,\parallel c}$ and the irreversibility field $H_{irr}$ in Li$_{0.17}$ZrNCl and Li$_{0.15}$THF$_{0.08}$ZrNCl. $H_{c2,\parallel c}$ was obtained from magnetization measurements (abbreviated as M in the figure), and $H_{irr}$ from magnetization and TF-$\mu$SR measurements. The broken lines show a fit to the functional form of $H_{c2}$ given in the text.
FIG. 11. Temperature dependence of the resistivity of Li$_{0.17}$ZrNCl under external magnetic field for two sets of the field and current directions, measured using a four-probe contact. The applied fields range from 0 to 9 T, in the intervals of 1 T.
FIG. 12. Temperature dependence of the upper critical field $H_{c2}$ of Li$_{0.17}$ZrNCl, obtained from magnetoresistance.
TABLES

TABLE I. Synthesis method (see the text for details), stacking unit distance \(c_0/3\), superconducting transition temperature \(T_c\), estimated from magnetization, magnetic field penetration depth \(\lambda_{ab,\mu SR}(T \rightarrow 0)\) at zero temperature limit estimated from TF-\(\mu SR\), Ginzburg-Landau parameter \(\kappa\), upper critical field at zero temperature \(H_{c2, // c}(0)\), coherence length at zero temperature \(\xi_{ab}(0)\), and magnetic penetration depth at zero temperature \(\lambda_{ab,M}(0)\) estimated from reversible magnetization for intercalated HfNCl and ZrNCl systems reported in the present work. TF-\(\mu SR\) and magnetization measurements were performed under the magnetic field parallel to the \(c\)-axis.

| Sample          | Synthesis method | \(c_0/3\) | \(T_c\) | \(\lambda_{ab,\mu SR}(T \rightarrow 0)\) | \(\kappa\) | \(H_{c2, // c}(0)\) | \(\xi_{ab}(0)\) | \(\lambda_{ab,M}(0)\) |
|-----------------|------------------|-----------|---------|----------------------------------------|-----------|----------------------|------------------|---------------------|
| \(\text{Li}_{0.17}\text{ZrNCl}\) | (i) \(n\)-Butyllithium | 9.4       | 14.2    | 3700                                   | 56        | 4.7                  | 83               | 4700                |
| \(\text{Li}_{0.4}\text{ZrNCl}\) | (i) \(sec\)-Butyllithium | 9.4       | 12.5    | 3900                                   |           |                      |                  |                     |
| \(\text{Li}_{0.6}\text{ZrNCl}\) | (i) \(tert\)-Butyllithium | 9.4       | 11.7    |                                         |           |                      |                  |                     |
| \(\text{Li}_{0.15}\text{THF}_{0.08}\text{ZrNCl}\) | (ii) THF          | 13.3      | 14.4    | 5200                                   | 76        | 4.2                  | 88               | 6700                |
| \(\text{Li}_{0.18}\text{PC}_{0.15}\text{ZrNCl}\) | (ii) PC           | 13.3      | 14.6    |                                         |           |                      |                  |                     |
| \(\text{Li}_{0.24}\text{THF}_{0.14}\text{HfNCl}\) | (iii) 8 \(mM\) Li-Naph | 13.3      | 25.5    |                                         |           |                      |                  |                     |
| \(\text{Li}_{0.5}\text{THF}_{0.3}\text{HfNCl}\) | (iii) 100 \(mM\) Li-Naph | 18.7      | 25.5    |                                         |           |                      |                  | 3900                |