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Upper critical field in the electron-doped layered superconductor $ZrNCl_{0.7}$: Magnetoresistance studies

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We report magnetoresistance measurements of layered superconductor $ZrNCl_{0.7}$ at high magnetic fields (H) as high as 27 T and temperatures (T) as low as 0.5 K. The T dependence of the upper critical field $H_{c2}(T)$ for $H \parallel c$ and $H \perp c$ was obtained. $H_{c2}(T)$ starts to increase with a gentle slope near $T_c(0)$ followed by a steep slope with decreasing T, implying the dimensional crossover of the interplane coherence length from three dimensional to two dimensional (2D). The $H_{c2}(T)$ is found to be anisotropic for the field direction, where the slope of $H'_{c2}=(dH_{c2}/dT)$ near $H \approx 1$ T can be estimated as $H'^{\perp}_{c2} \approx -22.1$ kOe/K and $H'^{\parallel}_{c2} \approx -4.9$ kOe/K for $H \parallel c$ and $H \perp c$, respectively. The obtained anisotropy parameter $\gamma \approx 4.5$ gives evidence for the 2D characteristic of the superconducting state in $ZrNCl_{0.7}$.

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Layer-structured β-MNCl (M=Hf,Zr), which is an insulator having a band gap of ~4.3–5 eV, was found to change into a superconductor with a small amount of alkali intercalation.[1] The highest superconducting transition temperature, $T_c \sim 25.5$ K, was recorded for $Li_{0.48}(THF)_yHfNCl$ (THF; tetrahydrofuran C_4H_8O). Recently, Zhu and coworkers found that an insulating β-MNCl becomes superconducting through partial deintercalation of the chlorine layers.[3] These systems have layered structure stacking of Cl-[MN]-[NM]-Cl slabs along the c axis perpendicular to the slab.[2] Recent experimental[4,5] and theoretical studies[6–8] have demonstrated a two-dimensional (2D) electronic state for which the superconductivity is derived from the 2D double [MN] honeycomb network. An unusual superconducting mechanism has been suggested.[9–12] Ito *et al.* claimed that the 2D superfluid density n_{s2D}/m^*_{ab} (superconducting carrier density/effective mass) is a dominant determining factor for the high T_c in MNCl superconductors from μSR results.[13]

The anisotropy of the upper critical field $H_{c2}(T)$ was first reported for Li-doped HfNCl.[4] However, lack of experimental data renders it impossible to discuss the T dependence of H_{c2} at $T \to 0$. Furthermore, T_c=25.5 K for Li-doped HfNCl is too high to determine the whole H_{c2} versus T phase. Recently, Ito *et al.* reported that the anisotropy ratio of H_{c2} for $H \perp c$ ($H^{\perp}_{c2}$) to that for $H \parallel c$ ($H^{\parallel}_{c2}$) in $Li_{0.17}ZrNCl$ is roughly 3 (Ref. 13). The entire H_{c2} versus T phase, however, has not been put forth yet. Together with results of Li-HfNCl (Refs. 4 and 9), the characteristics of the 2D superconducting state are believed to be important for the electron-doped MNCl system. Further measurements are required to clarify the intriguing superconducting properties in MNCl superconductors. In this sense, the studies of $ZrNCl_{0.7}$ or Li_xZrNCl having lower $T_c \sim 13$ K might allow us to cover the whole H_{c2} versus T phase diagram, thereby bringing about intrinsic behavior of the quasi-2D superconductors. For those reasons, this study is intended to determine the H_{c2} versus T phase diagram for Cl-deintercalated β-ZrNCl ($ZrNCl_{0.7}$) with $T_c \sim 13$ K.

Details of sample preparation and characterization for $ZrNCl_{0.7}$ have been reported elsewhere.[14] The powder sample was pressed into pellet form to orient ZrN planes (ab plane) under 1.5 kbar (150 MPa) in argon atmosphere.[4] Four oriented pellets, Nos. 1–4 were thus prepared. X-ray rocking curve measurements revealed that the ab plane of the crystals were oriented in the pellets with full width at half maximum (FWHM) of less than 7°. Resistivity measurements were carried out using a four probe dc/ac method in the T range of 0.5–300 K. Here, the samples were treated carefully in a glove box with high-purity He gas. The current and voltage leads were connected to the sample using silver paste with a toluene solvent; then they were covered with epoxy (stycast 1266) to prevent their degradation by exposure to moisture and oxygen. A magnetic field was provided by a conventional solenoid-type superconducting magnet in the field range of H=0–15 T, and by a hybrid magnet up to H=27 T at the High Field Laboratory for superconducting materials, IMR, Tohoku University. We also confirmed magnetization characteristics at various fields up to 5 T. Magnetization measurements showed that the substantial diamagnetic signals become apparent as the magnetic field increases above 1 T (not shown). These features are qualitatively identical to those for Li-HfNCl reported previously,[4] in which the lowest-Landau-level (LLL) scaling analysis for the 2D superconducting fluctuations was adopted.[15]

Figure 1 shows typical interplane resistivity ρ_c for the current direction of $I \parallel c$ (hereafter denoted as I_c) for sample No. 4 and in-plane resistivity ρ_{ab} for $I \perp c$ (hereafter denoted as I_{ab}) for sample No. 2. The negative slope of resistivity $d\rho(T)/dT<0$ was observed in the normal state near T_c. Similar behavior of the T dependence of resistivity was observed previously in $Li_{0.17}ZrNCl$ by Ito *et al.*;[13] that study indicated that $d\rho(T)/dT<0$ is not intrinsic, but rather extrinsic because of grain boundaries. Actually, $d\rho(T)/dT<0$ of

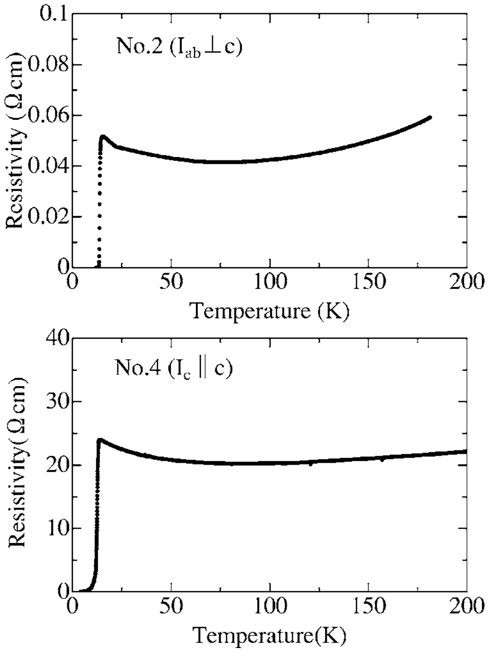

FIG. 1. Temperature dependence of interplane resistivity ρ_c ($I \| c$, sample No. 4) and inplane resistivity ρ_{ab} ($I \perp c$ sample No. 2).

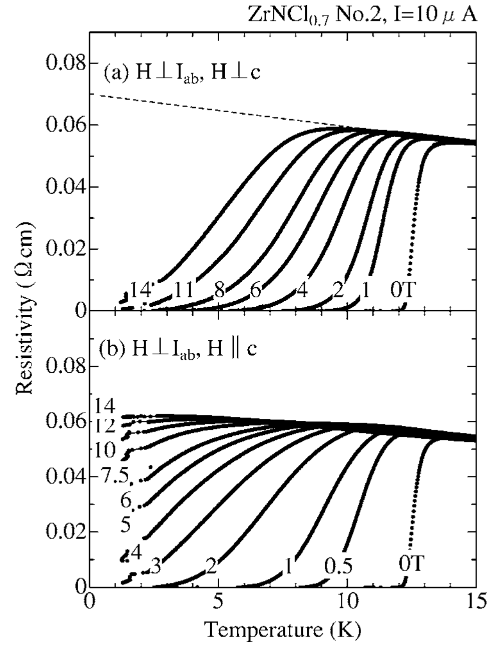

FIG. 3. Temperature dependence of the resistivity of $ZrNCl_{0.7}$ for $H \perp c$ and $H \| c$ for various magnetic fields. The dashed line in (a) represents the linear extrapolation of the normal-state resistivity.

the present $ZrNCl_{0.7}$ depends strongly on the sample, but T_c hardly depends on it.

The remarkable feature in $\rho(T)$ is that the interplane resistivity $\rho_c(T)$ is about one hundred times larger than the in-plane resistivity $\rho_{ab}(T)$, i.e., $\rho_c/\rho_{ab} \approx 10^2$, but it is difficult to evaluate the absolute value of ρ_c accurately because of experimental problems including the terminal connection for the fragile pellet, anaerobiotic character, and misalignment effects. This feature indicates that the charge transfer between the layers is weak, being consistent with the 2D character of the electronic structure.[4–8] Similar but more pronounced anisotropy of resistivity has been reported for layered organic superconductors, e.g., $\rho_c/\rho_{ab} \approx 10^3$ in κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$. (Ref. 16).

Figure 2 depicts the field-angle dependence of the resistivity at $H=8$ T and $T=8$ K. A clear but broad dip of the resistivity was observed for sample No. 2, reflecting the anisotropy of the superconducting state. Similar behavior was observed in other samples. Such broad dips indicate a considerably misaligned orientation. Although the x-ray rocking curve measurement indicated the highly oriented characteristic of the sample, it might overestimate the grain alignment in this pellet.

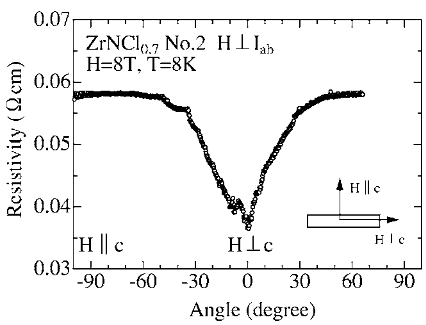

FIG. 2. Field-angle dependence of resistivity for $H=8$ T and $T=8$ K.

The T dependence of the resistivity under different magnetic fields with $H \| c$ and $H \perp c$ is shown in Fig. 3. As mentioned previously, the observed superconducting transition for $H \perp c$ might be broadened by both the grain boundaries and misalignment effects. On the other hand, we note here that, for $H \| c$, the respective broadenings of the resistive transitions are more remarkable than that for $H \perp c$; substantial suppression of $T_c(H)$ is observed. These features are consistent with results of magnetization measurements near T_c. Such broadening of the superconducting transitions in resistivity and magnetization for $H \| c$ is typical of low- dimensional superconductors. It is a natural consequence of the existence of superconducting fluctuations.[4,15]

Figure 4 shows magnetoresistance for $H \perp c$ and fields up to 27 T at different temperatures from $T=13$ to 0.5 K. The dashed line in the figure is the line expected from the linear extrapolation of the normal-state resistivity in Fig. 3(a). As mentioned in the previous text, the broad resistive transitions might be ascribed to both the grain boundaries and misalignment effects.

The T dependence of the $H_{c2}(T)$ for $H \perp c$ and $H \| c$ is illustrated in Fig. 5. Here, T_c is tentatively defined by an 80% level of the normal-state resistivity because the broad resistive transitions prevent the exact determination of $T_c(H)$. For that reason, the zero-field transition temperature, $T_c(0)$, can be estimated as $T_c(0) \approx 12.8$ K. Results showed that $H_{c2}(T)$ starts to increase with a gentle slope near $T_c(0)$ followed by a steep one with decreasing T. Such distinct behavior has been observed in other layered superconductors and is ascribable to the dimensional crossover from three-

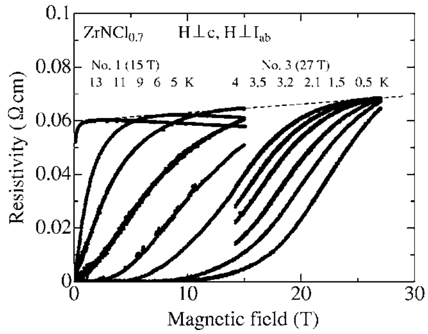

FIG. 4. Magnetoresistance $\rho(H)$ at selected temperatures. In the T range of 4–13 K, $\rho(H)$ was measured for sample No. 1 using a solenoid-type superconducting magnet; in the T range of 0.5–4 K, $\rho(H)$ was measured for sample No. 3 using the hybrid magnet. The dashed line in the figure is the line expected from linear extrapolation of the normal-state resistivity in Fig. 3(a).

dimensional (3D) to 2D caused by T dependence of the coherence length $\xi(T)$. Under high magnetic fields that are stronger than 1 T, the slope $H'_{c2}=(dH_{c2}/dT)$ yields a value of $H'^{\perp}_{c2}\approx-22.1$ kOe/K and $H'^{\parallel}_{c2}\approx-4.9$ kOe/K, respectively. The value of $H^{\parallel}_{c2}(0)$ is expected to be less than ≈ 7 T, and is consistent with previous results by Ito *et al.*[13]

In general for layered superconductors, either the anisotropic Ginzburg-Landau (GL) model[17] or the 2D Lawrence-Doniach (LD) model[18] can be utilized, depending on the interlayer interaction in which the crossover from the LD to the GL regimes occurs at the boundary condition of $\xi_c=d/\sqrt{2}$ with interlayer spacing d. The anisotropy parameter γ of the anisotropic GL model can be estimated as $\gamma=H'^{\perp}_{c2}/H'^{\parallel}_{c2}\approx 4.5$, which is direct evidence for quasi-2D aspects of the superconducting state. The GL coherence length ξ is calculated as $\xi_{ab}\approx 71$ Å and $\xi_c\approx 16$ Å, using relations $-H'^{\parallel}_{c2}T_c\approx\phi_0/(2\pi\xi^2_{ab})T_c$ and $\gamma=\xi_{ab}/\xi_c$ (Ref. 17).

We next compare with Li-doped HfNCl homologue. In Li-HfNCl, $\xi_c\approx 15.9$ Å is shorter than $d\approx 19$ Å, indicating Josephson coupling between the adjacent layers.[4] In addition,

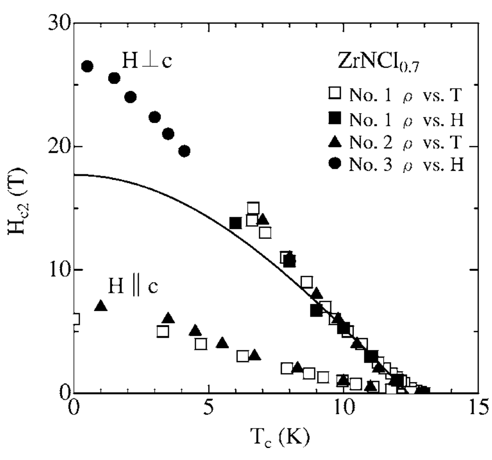

FIG. 5. Temperature dependence of the upper critical field H_{c2} for $H\perp c$ and $H\parallel c$. The transition temperature $T_c(H)$ was determined by the 80% level of the normal-state resistivity. The solid line represents the curve calculated using the WHH theory for 3D superconductors (see text).

^{7}Li, ^{39}Cl, and ^{15}N NMR Knight-shift studies clarified that superconductivity is derived from the HfN layer.[4,9,10] It is noteworthy that $\gamma\approx 4.5$ for ZrNCl is larger than $\Gamma\approx 3.7$ for the Li-HfNCl homologue.[4] Within the framework of the anisotropic GL model, we expect γ(ZrNCl) < γ(Li-HfNCl) using the relations of d(ZrNCl) < d(Li-HfNCl) and ξ_c(ZrNCl) ~ ξ_c(Li-HfNCl).[4] On the other hand, the experimental result, γ(ZrNCl) > γ(Li-HfNCl), implies that the superconductivity of MNCl is independent of the interlayer spacing. Actually, the μSR studies for a Li-doped ZrNCl system by Ito *et al.*[13] also demonstrated that T_c, ξ_{ab} and n_s/m^* are independent of the interlayer distance, suggesting a highly 2D character of the superconductivity in MNCl. As mentioned previously, both the grain boundaries and misalignment effects are inevitable in the present sample, where misalignment by several degrees would lower the measured $H_{c2}(0)$ by several tesla.[19] If the upturn of the $H_{c2}(T)$ curve in the vicinity of $H=0$ is attributable to the 3D-2D crossover, a more realistic value of ξ_c of $ZrNCl_{0.7}$ would be several angstrom; the estimated $H^{\perp}_{c2}\sim 27$ T might be underestimated, implying that $\gamma>4.5$.

We found that the observed $H^{\perp}_{c2}(T)$ decreases linearly as T_c-T at $T\to 0$. The Werthamer-Helfand-Hohenberg (WHH) theory predicts that $H_{c2}(T)$ at $T\to 0$ K is fundamentally determined by the initial slope of the H_{c2} versus T curve, but is suppressed as $H_{c2o}=a(-dH_{c2}/dT)_{T_c}T_c$ ($a=0.73$ for clean limit; $a=0.69$ for dirty limit) by the orbital pair-breaking effect.[20,21] Furthermore, for spin-singlet superconductors, H_{c2} is suppressed by the Pauli paramagnetic pair-breaking limit defined by $H_p=\Delta/\sqrt{2}\mu_0$, where Δ and μ_0 are the superconducting energy gap and the magnetic moment of electrons.[22–24]

If we apply the WHH theory for the clean limit case to $H^{\perp}_{c2}$ of the present system, $H_{c2o}(0)$ can be estimated as ≈ 18.4 kOe using $H'^{\perp}_{c2}=-22.1$ kOe/K. We can also estimate the BCS Pauli limit as $H_p\approx 23.5$ T with $T_c=12.8$ K and $2\Delta=3.5k_BT_c$. The solid line in Fig. 5 is the theoretical curve expected from the WHH relation for 3D superconductors. Within the conventional BCS framework, the relation of $H_p>H_{c2o}(0)$ suggests that $H^{\perp}_{c2}$ should be limited by the orbital effect, i.e., $H_{c2o}(0)$. For a layered superconductor in the LD regime, on the other hand, when the field is applied parallel to the plane ($H\perp c$), the kinetic energy of the orbital motion of the pairs caused by the magnetic field is depressed because of the weak electron transfer between layers. Consequently, the orbital limit becomes much higher than the expected value from the WHH relation. Although the obtained $H^{\perp}_{c2}(0)$ seems to break through $H_p=23.5$ T, it can be reconciled by taking account of either the strong-coupling effect, $2\Delta=5k_BT_c$ (Ref. 25), or reduction of the g factor. It is worth emphasizing that the observed T dependence of $H^{\perp}_{c2}(T)$ is ascribable to the 2D character of the superconducting state.

In summary, we have measured the resistivity of oriented polycrystals $ZrNCl_{0.7}$. Magnetoresistance measurements have demonstrated anisotropic superconducting properties of the present material, which closely resemble those of the Li-doped HfNCl. The estimated anisotropy parameter

$\gamma \approx 4.5$ gives evidence for a 2D characteristic of the superconducting state in $ZrNCl_{0.7}$. The present studies were performed for oriented pellets, not for single-crystals, which would engender underestimation of the anisotropy of the superconductivity. Measurements using single-crystal samples are necessary to clarify the anisotropy of the superconducting state.

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