A number of superconductors have been synthesized by doping FeSe solids with metal atoms, establishing that this is a very effective way to realize alternative superconductors [1–15]. The metal doping has been achieved using a high-temperature annealing technique [1–6], a liquid solution technique [7–14], and an electrochemical technique [15]. However, the metal doping of FeSe1−yTe5, where y ≠ 0, has only been reported in a few studies, in which doping was performed using the annealing and liquid solution techniques [16–18].

Solid FeSe showed a Tc as high as 8 K [19,20], while the Tc value of FeSe1−yTe5 made a domelike curve when plotted against z. The maximum Tc was 14 K for z = 0.5 in FeSe1−yTe5 [21]. Bulk FeTe crystals did not display superconductivity. This phase diagram attracted much attention because of the expectation that a high-Tc phase would be realized by the metal doping of FeSe0.5Te0.5. Sakai et al. doped FeSe0.5Te0.5 with various metal atoms using the liquid NH3 technique [16], which provided Tc’s of 17 K for (NH3)0.63(Ca0.4FeSe0.5)Te5, 21 K for (NH3)0.63Na0.4FeSe0.5Te0.5, and 26 K for (NH3)0.63Li0.4FeSe0.5Te0.5. Lei et al. investigated the z dependence of Tc in (NH3)xFeSe1−yTe5 (0 ≤ z ≤ 0.8, M: Li and Na), and a Tc of 21 K was observed for (NH3)xNa5FeSe0.5Te0.5 [18]. They determined the NH3 quantity (x) to be 0.3–0.8 using liquid chromatography.

Recently, we discovered multiple superconducting phases in (NH3)xNa5FeSe0.5Te0.5 [13], indicating that the Na atom occupies the on-center position (2a site) in the I4/mmm structure (on-center structure) when the x value is small, while the Na atom occupies the off-center position (2b site) in the I4/mmm lattice (off-center structure) when the x value is large. The lattice constant (c), which is larger in the off-center structure, which provided the high-Tc phase.

In this study we discovered a superconducting phase of (NH3)xNa5FeSe0.5Te0.5 with a Tc as high as 27 K. There are at least two superconducting phases of (NH3)xNa5FeSe0.5Te0.5, with Tc values as high as 21 and 27 K, a property shared with (NH3)xNaFeSe. The x dependence of Tc was investigated in (NH3)xNa5FeSe0.5Te0.5, as well as the physical properties and crystal structure of the high-Tc phase of (NH3)xNa5FeSe0.5Te0.5. The stability of the just-discovered high-Tc phase was also checked. The temperature (T) dependence of resistance (R) was recorded for both phases (Tc = 21 K and Tc = 27 K) of (NH3)xNa5FeSe0.5Te0.5, and the critical magnetic fields (Hc) of both phases were determined from their R versus T plots. Based on the Tc and c values of (NH3)xNa5FeSe0.5Te0.5, the Tc versus c phase diagram was obtained, which was similar to that of metal-doped FeSe.

The β-FeSe0.5Te0.5 sample was prepared using the same method as that described in Ref. [16]. The samples of (NH3)xNa5FeSe0.5Te0.5 were prepared using the liquid NH3 technique [16]; the detailed experimental procedure was described in our previous report [16]. The magnetic susceptibility, M/H, of the samples was measured using a SQUID magnetometer (Quantum Design MPMS2); M and H refer to magnetization and applied magnetic field, respectively. The Tc and shielding fraction were 14.0 K and 100% at 2 K, respectively, for FeSe0.5Te0.5 (not shown).

The R of the samples was recorded in standard four-terminal measurement mode with a He cryostat regulated by a temperature controller (Oxford Instruments ITC503); the H was applied using an Oxford superconducting magnet system with variable temperature insert; the electric current (I) was supplied by a Keithley 220 programmable current source, and the voltage was measured by a Keithley Nanovoltmeter 2182. Four conducting wires for the R measurement were attached to each pellet of the high-Tc and low-Tc phase of (NH3)xNa5FeSe0.5Te0.5 using silver paste (see Fig. S1 in the Supplemental Material [22]); the pellet was prepared at room temperature. The x-ray powder diffraction (XRD) patterns of the samples were measured with a Rigaku R-Axis Rapid-NR x-ray diffractometer with Mo Ka source (wavelength λ = 0.71078 Å). The chemical composition of each sample was...
determined by energy dispersive x-ray (EDX) spectroscopy with an EDX spectrometer equipped with a scanning electron microscope (SEM) (Keyence VE-9800–EDAX Genesis XM2). Throughout this paper, the stoichiometric compositions of the samples prepared are expressed as the experimental nominal values, and the stoichiometric compositions of only two samples were experimentally determined. In this paper, the chemical formula of the samples described without additional comment refers to the experimental nominal values.

The $M/H$ versus $T$ plots of (NH$_3$)$_y$Na$_x$FeSe$_{0.5}$Te$_{0.5}$ are shown in Fig. 1(a). The $T_c^{\text{inset}}$ and $T_c$ values were determined to be 28 and 27 K, respectively. The shielding fraction was 89% at 2 K; i.e., it was the high-$T_c$ phase. The XRD pattern was analyzed by Le Bail fitting considering two phases, the high-$T_c$ and low-$T_c$ phases, respectively. The ticks (pink and purple) refer to the positions of the high-$T_c$ and low-$T_c$ phases, respectively. The green and blue curves refer to the background and the difference between the experimental and calculated XRD patterns, respectively.

$H_{c1}$ was determined to be 200 Oe from the expanded $M$ versus $H$ plot shown in the inset of Fig. 1(b), which is higher than that (100 Oe) of the low-$T_c$ phase [16]. Here, it should be noticed that the $M$ plotted in Fig. 1(b) is smaller by a factor of 5 than that predicted from the $M/H-T$ plot shown in Fig. 1(a). We do not know why the $M$ becomes smaller than that predicted from Fig. 1(a). After the measurement of the $M$-$H$ curve [Fig. 1(b)], the $M/H-T$ plot was recorded again, which showed the same $M/H-T$ plot as that shown in Fig. 1(a), indicating no sample degradation. Anyway, as the $M$-$H$ curve suggests a linear variation of $M$ against $H$ up to 200 Oe, we concluded that 200 Oe is a reasonable value for $H_{c1}$ in the high-$T_c$ phase.

Figure 1(c) shows the EDX spectrum of the high-$T_c$ phase of (NH$_3$)$_y$Na$_x$FeSe$_{0.5}$Te$_{0.5}$; the same sample was used for Figs. 1(a) and 1(b). The stoichiometric composition of the (NH$_3$)$_y$Na$_x$FeSe$_{0.5}$Te$_{0.5}$ sample was experimentally determined to be (NH$_3$)$_{y_{\text{Na0.63Fe0.55Se0.55}}}$Te$_{0.44(2)}$, in which $y = 0.61(4)$, i.e., (NH$_3$)$_{61(4)}$Na$_{63(5)}$Fe$_{85}$Se$_{55(5)}$Te$_{0.44(2)}$, where the Fe count was expressed as 0.85 so that the sum of Se and Te would be equal to 1.0. We confirmed that the $y$ value fell within the range 0.6–0.7, using three different samples (high-$T_c$ phase).

The XRD pattern of (NH$_3$)$_y$Na$_x$FeSe$_{0.5}$Te$_{0.5}$ is shown in Fig. 1(d); the sample was not that used for Figs. 1(a)–1(c), but its $T_c$ was 30 K and the shielding fraction was 89% at 2 K; i.e., it was the high-$T_c$ phase. The XRD pattern was analyzed by Le Bail fitting considering two phases, the high-$T_c$ phase and low-$T_c$ phase, the major phase being the high-$T_c$ phase. The space group was $I4/mmm$ for both phases. The lattice constants $a$ and $c$ for the high-$T_c$ phase were determined to be 3.874(2) and 19.33(1) Å, respectively. A trace of low-$T_c$ phase was observed in the XRD pattern, and $a$ and $c$ were 4.029(2) and 16.84(1) Å, respectively. However, the $c$ value was significantly different from the $c (=17.798(7)$ Å) of the low-$T_c$ phase reported previously [16], indicating that the exact $c$ value could not be determined because so little of the low-$T_c$ phase was contained in the sample. The $a$ of the low-$T_c$ phase reported previously was 3.9822(6) Å. Reliable values of $a$ and $c$ for the low-$T_c$ phase are described later.

The high-$T_c$ and low-$T_c$ phases of (NH$_3$)$_y$Na$_x$FeSe were selectively prepared by varying the concentration of intercalated Na atoms, i.e., the $x$ value [13]. The high-$T_c$ phase in (NH$_3$)$_y$Na$_x$FeSe was obtained with high $x$ values, while the low-$T_c$ phase was produced in samples with low $x$ values. Figure 2(a) shows the $T_c$ values of the (NH$_3$)$_y$Na$_x$FeSe$_{0.5}$Te$_{0.5}$ samples prepared with various experimental nominal $x$ values. Two clearly distinguished $T_c$ values ($T_c = 28$ K and $T_c = 21$ K) were recorded for the (NH$_3$)$_y$Na$_x$FeSe$_{0.5}$Te$_{0.5}$ samples, although some scattering around the above values was observed. However, no clear correlation between $T_c$ and $x$ was found from the $T_c$ versus $x$ plot shown in Fig. 2(a). Here, it should be noticed that the $x$ corresponds to the experimental nominal value. Therefore, we may need to consider the difference between nominal and actual $x$ values for understanding why there is no clear correlation [Fig. 2(a)]. From the plot shown in Fig. 2(a), only a presence of two different $T_c$’s was clearly found in (NH$_3$)$_y$Na$_x$FeSe$_{0.5}$Te$_{0.5}$.
Figure 2(b) shows the $M/H$ versus $T$ curves of the typical low-$T_c$ phase of (NH$_3)_y$Na$_{0.5}$FeSe$_{0.5}$Te$_{0.5}$. The $T_c$ values were determined to be 23 and 21.5 K from the $M/H$ versus $T$ curve recorded in zero field cooled (ZFC) mode [Fig. 2(b)]. The shielding fraction was 28% at 10 K for this sample. Figure 2(c) shows the EDX spectrum of the low-$T_c$ phase, indicating chemical stoichiometry of (NH$_3$)$_{0.031}$Na$_{0.71}$Fe$_{1.33}$Se$_{0.489}$Te$_{0.525}$. The value of Fe was set at 1.33 so that the sum of Se and Te would be 1.0, as was done for the high-$T_c$ phase. The amount of NH$_3$ (y value) was determined to be 0.03(1) from the mass difference before and after reaction with liquid NH$_3$. Consequently, the amount of NH$_3$ is too small in the low-$T_c$ phase.

The XRD pattern of the low-$T_c$ phase, (NH$_3$)$_{0.4}$Na$_{0.6}$FeSe$_{0.5}$Te$_{0.5}$, is shown in Fig. 2(d). The XRD was analyzed by Le Bail fitting considering two phases, the low-$T_c$ phase and pristine FeSe$_{0.5}$Te$_{0.5}$. The major phase was the low-$T_c$ phase, and the $a$ and $c$ were determined to be 3.9824(6) and 17.787(7) \(\text{Å}\), respectively, which are consistent with the values $a = 3.9822(6) \text{Å}$ and $c = 17.798(7) \text{Å}$ reported previously for the low-$T_c$ phase [16]. The $c$ of the high-$T_c$ phase is larger by 1.543 \(\text{Å}\) than that of the low-$T_c$ phase, indicating that a larger $c$ produces a higher $T_c$, as also observed in (NH$_3$)$_y$M$_x$FeSe ($M$: alkali and alkali earth metal atoms) [9,12,13]. The space group is the same in the high-$T_c$ and low-$T_c$ phases, indicating that only the location of Na is different in each, as previously discussed for (NH$_3$)$_y$Na$_{0.5}$FeSe$_{0.5}$ [13]; we previously suggested that the Na occupies the on-center position in the low-$T_c$ phase and the off-center position in the high-$T_c$ phase, under the space group of $I4/mmm$. Therefore, we substantially assume the same scenario for the high-$T_c$ and low-$T_c$ phases of (NH$_3$)$_y$Na$_{0.5}$FeSe$_{0.5}$Te$_{0.5}$. On the other hand, Sedlmaier et al. suggested the primitive tetragonal structure ($P4/n$ or $P4/mmm$) for NH$_3$-rich $M_x$FeSe ($M$: Li, K, and Rb), with more expanded FeSe plane spacing than that in the body-centered tetragonal structure ($I4/mmm$) [10]. At the present stage, we cannot conclude whether the high-$T_c$ phase of (NH$_3$)$_y$Na$_{0.5}$FeSe$_{0.5}$Te$_{0.5}$ (NH$_3$-rich structure) takes such a primitive tetragonal structure. More detailed analysis using Rietveld refinement is necessary to determine the precise crystal structure.

The $M/H$ versus $T$ plot for (NH$_3$)$_y$Na$_{0.5}$FeSe$_{0.5}$Te$_{0.5}$ ($T_c = 27$ K and shielding fraction = 18% at 10 K) is shown in Fig. 3(a), and can be assigned to the high-$T_c$ phase. However, the $M/H$ versus $T$ plot changed drastically after 3 days, as shown in Fig. 3(b). The $T_c$ changed to 20 K from 27 K, implying conversion from the high-$T_c$ to the low-$T_c$ phase, indicating that the high-$T_c$ phase is a metastable phase. Such a conversion was frequently observed in this study. Therefore, it is necessary to investigate the physical properties of the high-$T_c$ phase quickly, before the conversion. No conversion was found on a scale of several days in (NH$_3$)$_y$Na$_{x}$FeSe, although no investigation of conversion was performed for longer time scales, such as a year.

The temperature dependence of $R$ for the high-$T_c$ and low-$T_c$ phases at different $H$’s is presented in Figs. 4(a) and 4(b), respectively. The $T_c$ and $T_c$ values were determined to be 31 and 27 K, respectively, from the $M/H$ versus $T$ plot for the high-$T_c$ phase [inset of Fig. 4(a)], while they were 23 and 21 K for the low-$T_c$ phase [inset of Fig. 4(b)]. As seen from Figs. 4(a) and 4(b), zero $R$ was not observed for either phase because of the use of pellets fabricated from polycrystalline powder samples. No observation of zero $R$ is the same as that in Na- and Ba-doped FeSe prepared using liquid NH$_3$ [7]. As seen from Figs. 4(a) and 4(b), the $T_c$ and $T_c$ decrease monotonically in both phases with...
FIG. 4. Plots of $R$ versus $T$ for (a) high-$T_c$ and (b) low-$T_c$ phases of $(\text{NH}_3)_y\text{Na}_x\text{FeSe}_{0.5}\text{Te}_{0.5}$ at different $H$'s. In the insets of (a,b), plots of $M/H$ versus $T$ are provided to show the superconductivity of the samples. The applied $H$ are shown by solid circles with different colors. Plots of $H_c$ versus $T$ for (c) the high-$T_c$ and (d) low-$T_c$ phases determined from the $R$ versus $T$ plots recorded at different $H$'s. The fitted lines are linear best fits.

the application of increasing $H$. In other words, the onset of $R$ drop shifts to a lower temperature, indicating that the $R$ drop can be assigned to a superconducting transition. The $H_c$ versus $T$ plots for the high-$T_c$ and low-$T_c$ phases are provided in Figs. 4(c) and 4(d). The $H_c$ values at 0 K [$H_c(0)$] for the high-$T_c$ and low-$T_c$ phases were, respectively, evaluated to be 20 and 34 T with the Werthamer-Helfand-Hohenberg formula, $H_c(0) = -0.693T_c(dH_c/dT)_{T=T_c}$; the values of $H_c$ were 200 and 100 Oe for high-$T_c$ and low-$T_c$ phases, as described previously. London penetration depth ($\lambda$) and Ginzburg-Landau coherent length ($\xi(\lambda)$) are determined to be $1.8 \times 10^5$ and 4.1 nm for the high-$T_c$ phase, respectively, and $2.6 \times 10^5$ and 3.1 nm for the low-$T_c$ phase, using the formulas $H_c = \frac{\Phi_0}{\pi\xi^2}$, and $H_c = \frac{\Phi_0}{\pi\lambda^2}\ln\left(\frac{\lambda}{\xi}\right)$, where $\Phi_0(\approx 2.0678 \times 10^{-7} \text{ G cm}^2)$ is a quantum magnetic flux [23]. The values of the Ginzburg-Landau parameter, $\kappa$, were more than $1/\sqrt{2}$ for both phases, indicating that these phases are categorized as “type-II superconductor.”

Finally, the $T_c$ was plotted as a function of $c$ for $(\text{NH}_3)_y\text{M}_x\text{FeSe}$ and $(\text{NH}_3)_y\text{M}_x\text{FeSe}_{0.5}\text{Te}_{0.5}$ in Fig. 5, where $M$ represents alkali and alkali earth metal atoms, the plots are based on data in this paper and previous articles on various metal-doped FeSe and FeSe$_{0.5}$Te$_{0.5}$ (Refs. [7,9,12]), and the pressure dependence of $T_c$ in $(\text{NH}_3)_y\text{Cs}_x\text{FeSe}$ [24]. Previously, we showed a clear correlation between $T_c$ and $c$ for $(\text{NH}_3)_y\text{M}_x\text{FeSe}$, and the saturation of $T_c$ with more expanded FeSe plane spacing [9,12,13]. As seen from Fig. 5, the $T_c$ versus $c$ behavior for $(\text{NH}_3)_y\text{M}_x\text{FeSe}_{0.5}\text{Te}_{0.5}$ is similar to that of $(\text{NH}_3)_y\text{M}_x\text{FeSe}$, although the $T_c$ of the former is lower than that of the latter. Namely, in $(\text{NH}_3)_y\text{M}_x\text{FeSe}_{0.5}\text{Te}_{0.5}$, the $T_c$ increases with increasing $c$, as in $(\text{NH}_3)_y\text{M}_x\text{FeSe}$, in which it saturates or decreases at larger $c$. Here, we did not remark on the difference in carrier concentration between high-$T_c$ and low-$T_c$ phases, because no clear correlation between $x$ and $T_c$ was observed. Furthermore, we found only two superconducting phases even when changing $x$ continuously in $(\text{NH}_3)_y\text{Na}_x\text{FeSe}_{0.5}\text{Te}_{0.5}$ and $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$ [13], suggesting that a different $T_c$ may not originate from the difference in carrier concentration. In other words, the $T_c$ can be substantially scaled with the FeSe or FeSe$_{0.5}$Te$_{0.5}$ plane spacing. The increase in $T_c$ against $c$ can be simply explained by the improved Fermi-surface nesting allowed by the expanded FeSe or FeSe$_{0.5}$Te$_{0.5}$ layer spacing (or increase in two dimensionality), while the saturation and decrease in $T_c$ for the more expanded layer spacing implies that the extremely small interaction between layers has a negative effect on superconductivity; i.e., interaction between layers is required for the emergence of superconductivity. These properties of metal-doped Fe$_{1-x}$Te$_x$ superconductors may open an avenue for the realization of metal-doped Fe chalcogenide materials with higher $T_c$ values.

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