Emergence of Multiple Superconducting Phases in (NH₃)ₓMₓFeSe (M: Na and Li)

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We previously discovered multiple superconducting phases in the ammoniated Na-doped FeSe material, (NH₃)ₓNaₓFeSe. To clarify the origin of the multiple superconducting phases, the variation of Tc was fully investigated as a function of x in (NH₃)ₓNaₓFeSe. The 32 K superconducting phase is mainly produced in the low-x region below 0.4, while only a single phase is observed at x = 1.1, with Tc = 45 K, showing that the Tc depends significantly on x, but it changes discontinuously with x. The crystal structure of (NH₃)ₓNaₓFeSe does not change as x increases up to 1.1, i.e., the space group of I4/mmm. The lattice constants, a and c, of the low-Tc phase (Tc = 32.5 K) are 3.9120(9) and 14.145(8) Å, respectively, while a = 3.8266(7) Å and c = 17.565(9) Å for the high-Tc phase (~46 K). The c increases in the high Tc phase, implying that the Tc is directly related to c. In (NH₃)ₓLiₓFeSe material, the Tc varies continuously within the range of 39 to 44 K with changing x. Thus, the behavior of Tc is different from that of (NH₃)ₓNaₓFeSe. The difference may be due to the difference in the sites that the Na and Li occupy.

Any strategy for increasing the superconducting transition temperature (Tc) in metal-doped FeSe is a most exciting research subject, because the Tc can be effectively increased in metal-doped FeSe using a variety of methods such as ammoniation¹⁻⁵, pressure application⁶ and solvent intercalation⁷; FeSe corresponds to PbO-type FeSe, i.e., β-FeSe. The highest Tc reported in bulk superconductors of metal-doped FeSe is ~50 K, as recorded in Tl₀.₆Rb₀.₄Fe₁.₆₇Se₂ and K₀.₈Fe₁.₇Se₂ under high pressure; through this paper, the chemical representation of (NH₃)ₓMₓFeSe is used instead of (NH₃)ₓMₓ'Fe₂Se₂. Our representation refers to the primitive basis of the crystal. Therefore, x = x'/2. At ambient pressure, the highest Tc in metal-doped FeSe materials is 46 K for (NH₃)ₓNa₀.₅FeSe¹. In metal-doped FeSe, the Tc increases with an increase in the lattice constant c, or the plane spacing between FeSe layers. The insertion of NH₃ molecules or ammoniated metal coordinates between the FeSe layers can expand the c. The ammoniation and metal intercalation in FeSe (or the formation of (NH₃)ₓMₓFeSe) can be simultaneously achieved by dissolving metal and FeSe in liquid NH₃ at low temperature. Recently, we succeeded in synthesizing (NH₃)ₓMₓFeSe₀.₅Te₀.₅ using the liquid NH₃ technique⁸, and found that the Tc of (NH₃)ₓNa₀.₅FeSe₀.₅ is lower than that of the corresponding FeSe materials. Thus, the liquid NH₃ technique is applicable to the intercalation of metal atoms into various FeSe₁₋ₓTeₓ (0.0 ≤ x ≤ 1.0). The chemical doping of metal atoms and NH₃ or ammoniated metal coordinates provides the advantage of expanding the two-dimensional (2D) layer spacing, which may contribute to an improved Tc.

Recently, the presence of multiple superconducting phases has been clarified in (NH₃)ₓKₓFeSe and (NH₃)ₓNaₓFeSe. In (NH₃)ₓKₓFeSe, a high-Tc phase (Tc = 44 K) was discovered in addition to the low-Tc phase (Tc = 30 K)⁴. The x-dependence of Tc was found to involve a discontinuous change in Tc; the high-Tc phase was observed with low x values, and the low-Tc phase found with high x values. The Tc was

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correlated with \( c \), i.e., a smaller \( c \) resulted in a lower \( T_c \). Discovering the presence of multiple phases is significant because of the possibility that a phase with even higher \( T_c \) might be found, even in metal-doped FeSe compositions previously examined. This makes the search for multiple superconducting phases in other FeSe materials important and exciting.

As described above, we recently discovered a new superconducting phase (low-\( T_c \) phase; \( T_c = 31.5 \text{ K} \)) in addition to the high-\( T_c \) phase (\( T_c = 46 \text{ K} \)) reported previously in (NH\(_3\))\(_y\)Na\(_x\)FeSe. However, a systematic study on the origin of the different superconducting phases has not yet been performed, although a difference in \( c \) was found for the two phases. Also, the relationship between \( T_c \) and \( x \) has not yet been investigated in (NH\(_3\))\(_y\)Na\(_x\)FeSe. Here we systematically study the variation of \( T_c \) as a function of \( x \) in (NH\(_3\))\(_y\)Na\(_x\)FeSe. Furthermore, the lattice constants were determined for the superconducting phases realized at different \( x \)'s to clarify the correlation between \( T_c \) and lattice constants. The variation of \( T_c \) in (NH\(_3\))\(_y\)Li\(_x\)FeSe was also investigated as a function of \( x \). Some interesting points to be clarified are as follows: (1) the presence of multiple superconducting phases, (2) the discontinuous or continuous variation of \( T_c \), and (3) the origin of the variation of \( T_c \). In this study, the superconducting phases were identified in the (NH\(_3\))\(_y\)Na\(_x\)FeSe and (NH\(_3\))\(_y\)Li\(_x\)FeSe samples, so that the answers were provided for the above important points.

Results

Multiple superconducting phases in (NH\(_3\))\(_y\)Na\(_x\)FeSe. Figure 1(a),(b) show the \( M/H \) curves of typical low-\( T_c \) and high-\( T_c \) phases of (NH\(_3\))\(_y\)Na\(_x\)FeSe, respectively. In the former sample nominal \( x = 0.1 \), and in the latter nominal \( x = 1.0 \). These samples each contain a 'single phase', either low-\( T_c \) or high-\( T_c \); actually a trace of non-doped 2-FeSe (\( T_c = 8 \text{ K} \)) is found in Fig. 1(a). The \( T_{\text{onset}} \) and \( T_c \) were determined to be 35 and 32.5 K from \( M/H \) curves at ZFC for the low-\( T_c \) phase (Fig. 1(a)), while the \( T_{\text{onset}} \) and \( T_c \) were 47 and 46 K at ZFC for the high-\( T_c \) phase (Fig. 1(b)). How the \( T_c \) was determined is shown in the insets of Fig. 1(a),(b). The shielding fractions at 10 K were evaluated to be 30.5% for the low-\( T_c \) phase and 26% for the high-\( T_c \) phase.

Figure 1(c),(d) show the XRD patterns of the low-\( T_c \) and high-\( T_c \) phases of (NH\(_3\))\(_y\)Na\(_x\)FeSe, respectively. The \( T_{\text{onset}} \) and \( T_c \) for the former sample (nominal \( x = 0.2 \)) were determined to be 35 and 32.5 K, respectively, from the \( M/H \) curve (not shown) in ZFC mode, and the shielding fraction at 10 K was 18%. No high-\( T_c \) phase was observed in this sample, but non-doped \( \beta \)-FeSe was included in the sample. The latter sample (nominal \( x = 1.0 \)) is the same as that providing the \( M/H \) curve shown in Fig. 1(b); no low-\( T_c \) phase was observed in the \( M/H \) vs. \( T \) curve of this sample.

The \( a \) and \( c \) were determined to be 3.9120(9) \( \text{Å} \) and 14.1458(8) \( \text{Å} \), respectively, for the low-\( T_c \) phase (Fig. 1(c)), while the \( a \) and \( c \) were 3.8266(7) \( \text{Å} \) and 17.5659(9) \( \text{Å} \) respectively, for the high-\( T_c \) phase (Fig. 1(d)). The values of \( a \) and \( c \) were determined using LeBail fitting under the space group of 14/mmm, suggesting no change of crystal structure between the low-\( T_c \) and high-\( T_c \) phases. The \( a \) and \( c \) values for both the phases were close to those reported previously by our group (\( a = 3.891(2) \text{Å} \) and \( c = 14.269(4) \text{Å} \) for the low-\( T_c \) phase; \( a = 3.8275(6) \text{Å} \) and \( c = 17.579(5) \text{Å} \) for the high-\( T_c \) phase)\(^9\). Furthermore, the \( a \) and \( c \) for the high-\( T_c \) phase determined in this study are also consistent with those reported by Ying et al. (\( a = 3.7846(4) \text{Å} \) and \( c = 17.432(1) \text{Å} \))\(^1\). From the lattice constants, it has been concluded that a larger \( c \) produces a higher \( T_c \). This conclusion is supported by the relation between \( T_c \) and \( c \) found in (NH\(_3\))\(_y\)M\(_x\)FeSe materials with various \( M \).

X dependence of superconductivity in (NH\(_3\))\(_y\)Na\(_x\)FeSe. To clarify the exact stoichiometry of (NH\(_3\))\(_y\)Na\(_x\)FeSe samples prepared in this study, the energy dispersive X-ray (EDX) spectroscopy was measured. To confirm the accuracy and precision of \( x \) determined by EDX, the \( x \) was determined for a reference sample, NaCl (purity = 99.0%). The EDX of NaCl showed Na\(_{1.0(0)}\)Cl, which means that the EDX can provide the \( x \) value with high accuracy and precision. The typical EDX spectra of the samples containing low-\( T_c \) and high-\( T_c \) phases are shown in Figures S1 and S2 of Supplementary Information. The exact stoichiometric composition of the (NH\(_3\))\(_y\)Na\(_x\)FeSe sample (nominal composition of Na = 0.1) with \( T_c = 33.6 \text{ K} \) (low-\( T_c \) phase) was expressed as ‘(NH\(_3\))\(_y\)Na\(_{0.17(3)}\)FeSe’, while the exact stoichiometric composition of the (NH\(_3\))\(_y\)Na\(_x\)FeSe sample (nominal composition of Na = 1.0) with \( T_c = 45.1 \text{ K} \) (high-\( T_c \) phase) was ‘(NH\(_3\))\(_y\)Na\(_{1.0(0)}\)FeSe’. These results show the consistency between the nominal and actual stoichiometry. However, the stoichiometric compositions of some samples determined from EDX spectra deviated within 0.3 from the nominal compositions, suggesting the difficulty in making the target material using liquid reaction method. Therefore, we use the \( x \) values determined from the EDX spectroscopy for \( x \) dependence of \( T_c \) and \( c \) in (NH\(_3\))\(_y\)Na\(_x\)FeSe samples. Notably, the exact amounts of NH\(_3\) contained in the samples could not be determined from EDX. Furthermore, we can comment on Fe vacancy. The EDX provided the chemical composition of Fe as 0.80(5) for (NH\(_3\))\(_y\)Na\(_{0.17(3)}\)Fe\(_{1.0(0)}\)Se, i.e., it can be expressed as ‘(NH\(_3\))\(_y\)Na\(_{0.17(3)}\)Fe\(_{0.80(5)}\)Se’ if considering the Fe vacancy. The stoichiometry of Fe was 0.70–0.84 in all samples, suggesting that ~75% of 4\( d \) site is occupied by Fe atom. Through this paper, we do not show the exact stoichiometry of Fe for all samples because it does not change as a function of \( x \), i.e., it does not relate to the change of lattice parameters and \( T_c \).

The \( T_c \)'s of all (NH\(_3\))\(_y\)Na\(_x\)FeSe samples prepared in this study are plotted as a function of \( x \), as shown in Fig. 2(a); the \( x \) is determined from EDX spectroscopy. In the low-\( x \) region below 0.4, the low-\( T_c \) phase (\( T_c = 32 \text{ K} \)) predominates in the samples, and all the samples substantially contain either the low-\( T_c \)
(\(T_c = 32\) K) or high-\(T_c\) (\(T_c \sim 45\) K) phase, i.e., a predominant phase exists in each sample. The \(T_c\) of the low-\(T_c\) phase does not change throughout the entire \(x\) region. As seen from Fig. 2(a), the high-\(T_c\) phase tends to be produced in the high-\(x\) region. The \(T_c\) of the high-\(T_c\) phase does not change with an increase in \(x\), suggesting that \((\text{NH}_3)_y\text{Na}_0.1\text{FeSe}\) does not show solid solution-like behavior (continuous change of \(T_c\)), but discontinuous superconducting phases. Only a phase exhibiting high \(T_c\) (~45 K) is produced at \(x = 1.1\) in \((\text{NH}_3)_y\text{Na}_x\text{FeSe}\). At \(x = 0.5–0.9\), either low-\(T_c\) or high-\(T_c\) phase is observed. These results show that the higher \(T_c\) is realized in the samples with higher \(x\) values. In other words, the \(T_c\) can be controlled by changing the proportion of Na (or \(x\)) in \((\text{NH}_3)_y\text{Na}_x\text{FeSe}\). Here we briefly comment the amount of \(\text{NH}_3\).

In this study, the \(\text{NH}_3\) amount was detected for only the low-\(T_c\) phase by the mass difference before and after the ammoniation. The \(y\) value of the low-\(T_c\) phase was scattered in 0.2–0.6. Nevertheless, the presence of \(\text{NH}_3\) was evidenced for the low-\(T_c\) phase, which is fully discussed in the Discussion section.

Figure 1. \(M / H\) vs. \(T\) plots of (a) \((\text{NH}_3)_y\text{Na}_0.1\text{FeSe}\) (low-\(T_c\) phase) and (b) \((\text{NH}_3)_y\text{Na}_1.0\text{FeSe}\) (high-\(T_c\) phase) in ZFC and FC modes (\(H = 20\) Oe). Insets in (a) and (b) show the method used to determine \(T_c\). XRD patterns of (c) \((\text{NH}_3)_y\text{Na}_0.2\text{FeSe}\) (low-\(T_c\) phase) and (d) \((\text{NH}_3)_y\text{Na}_1.0\text{FeSe}\) (high-\(T_c\) phase); ‘\(x\)’ marks correspond to the experimental XRD patterns. Red and green lines refer to calculated patterns (LeBail fitting) and background, respectively. Ticks refer to the peak positions predicted. In (c), two phases ((\(\text{NH}_3)_y\text{Na}_0.2\text{FeSe}\) and \(\beta\)-FeSe) are used in LeBail fitting, while in (d), a single phase ((\(\text{NH}_3)_y\text{Na}_1.0\text{FeSe}\)) is used.
peak is small. Thus, the XRD peak discontinuously shifts from $2\theta = 5.80^\circ$ to $2\theta = 4.50^\circ$, which implies that only two structural phases exist, even when the $x$ value changes. In other words, a solid-solution like structure does not appear in the (NH$_3$)$_y$NaxFeSe material. The $x$ dependence of $c$ determined by a LeBail fitting for the XRD patterns is shown in Fig. 2(d), which provides a constant $c$ in the low-$T_c$ phase for $x = 0.3$ and 0.5 and a constant $c$ in the high-$T_c$ phase for $x = 0.5$ and 1.1. The $a$ is constant in the whole $x$ values, indicating that the observed variation in $T_c$ is not related to $a$, as seen from Fig. S3 of Supplementary Information.

**X dependence of superconductivity in (NH$_3$)$_y$Li$_x$FeSe.** Figure 3(a) shows the $M / H$ curves in ZFC and FC modes for (NH$_3$)$_y$Li$_x$FeSe at $x = 0.1$. Notably, the $x$ value is nominal because EDX cannot provide the exact stoichiometric composition of Li; the detection of Li peak was impossible in our EDX spectrometer because of the confined energy range. The $T_c^{\text{onset}}$ and $T_c$ were determined to be 42 and 39.5 K from $M / H$ curve at ZFC. The shielding fraction was evaluated to be 25.5% at 10 K. The $M / H$ vs. $T$ curve shows that this sample contains only a single superconducting phase. We made the (NH$_3$)$_y$Li$_x$FeSe samples ($x = 0.1$ to 0.9), and when their $M / H$ curves were measured, they showed only a single superconducting phase. The average $T_c$ ($<T_c>$), is plotted with the estimated standard deviation (esd) as a function of $x$ in Fig. 3(b); the $<T_c>$ was evaluated from three samples. The $<T_c>$ vs. $x$ plot shows a continuous variation. It slowly increases with increasing $x$ up to 0.7; $<T_c> = 43.5$ K, and decreases slightly from 0.7. The maximum $T_c$ ($= 44$ K) is observed at $x = 0.7$. However, the variation is at most 5 K. The dome-like behavior in $T_c$ vs. $x$ plot shown in Fig. 3(b) was not observed in (NH$_3$)$_y$Na$_x$FeSe. Thus, it has

![Figure 2](https://www.nature.com/scientificreports/)

**Figure 2.** (a) $T_c$ vs. $x$ plots for (NH$_3$)$_y$Na$_x$FeSe. $x$ is determined from EDX spectra of the samples. (b) XRD patterns of (NH$_3$)$_y$Na$_x$FeSe at $x = 0.3$, 0.5 and 1.1. (c) XRD peaks ascribable to 002 reflection of (NH$_3$)$_y$Na$_x$FeSe at $x = 0.3$, 0.5 and 1.1. (d) $c$ vs. $x$ plots in (NH$_3$)$_y$Na$_x$FeSe. Solid black and blue circles refer to low-$T_c$ and high-$T_c$ phases, respectively.
been concluded that the behavior of $T_c$ versus $x$ in (NH$_3$)$_y$M$_x$FeSe is completely different depending on whether $M$ = Na or Li. Although the nominal $x$ was used in the plot of (NH$_3$)$_y$LixFeSe, this conclusion should be reliable. The dome-like behavior of $T_c$ – $x$ (Fig. 3b) must be validated by the $T_c$ – $x$ plot using actual $x$ value which may be determined by neutron diffraction.

Figure 3(c) shows the XRD patterns of (NH$_3$)$_y$LixFeSe ($x$ = 0.1 to 0.9); $x$ is the nominal values. The XRD patterns of (NH$_3$)$_y$LixFeSe are the same in all $x$ regions. The XRD patterns could be reproduced with two phases of (NH$_3$)$_y$LixFeSe and small amounts of $\beta$-FeSe. The $c$ value, determined using LeBail fitting, gradually increases with increasing $x$ up to 0.5, and decreases monotonically, as seen from Fig. 3(d); the maximum $c$ ($=17.03(2)$ Å) is observed at $x = 0.5$; the typical LeBail fitting for the XRD pattern is shown in Figure S4 of Supplementary Information. The results show clearly that $T_c$ is correlated with $c$.

Compared with $c$ value, $a$ value is almost constant (see Figure S5 of Supplementary Information). As in (NH$_3$)$_y$Na$_x$FeSe, the larger $c$ provides the higher $T_c$ in (NH$_3$)$_y$LixFeSe, but the $c$ changes continuously in (NH$_3$)$_y$LixFeSe, in contrast to the $c$ vs. $x$ plot in (NH$_3$)$_y$Na$_x$FeSe. Thus, solid-solution like behavior is observed in both $T_c$ and $c$ in (NH$_3$)$_y$LixFeSe.

**Discussion**

Here we must consider why $c$ is different in the low-$T_c$ and high-$T_c$ phases. As shown for (NH$_3$)$_y$Li$_x$FeSe, with a $T_c$ as high as 43 K, the Li atoms occupy an off-center position in the $I4/mmm$ lattice (Fig. 4(a))

Specifically, the Li atoms occupy the 4c site (0,1/2,0) and 2b site (0,0,1/2). The $T_c$ (= 43 K)$^2$ and the $c$ ($= 16.5266(9)$ Å)$^2$ of (NH$_3$)$_y$LixFeSe are close to those of the high-$T_c$ phase ($T_c = 46$ K and $c = 17.565(9)$ Å)$^2$ of (NH$_3$)$_y$Na$_x$FeSe. The difference in $c$, $\Delta c$, between (NH$_3$)$_y$LixFeSe and the high-$T_c$ phase of (NH$_3$)$_y$Na$_x$FeSe may be due to the different ionic radii of Li and Na and consequent differences in local structure around...
M. If this is the case, it is tempting to conclude that the structure of the high-$T_c$ phase in $(\text{NH}_3)_y\text{NaxFeSe}$ may be the same as that of $(\text{NH}_3)_y\text{LixFeSe}$ (or off-center structure, Fig. 4(a)). The suggested structure of the high-$T_c$ phase in $(\text{NH}_3)_y\text{NaxFeSe}$ is shown in Fig. 4(b).

On the other hand, the $T_c$ ($=32.5$ K) of the low-$T_c$ phase in $(\text{NH}_3)_y\text{NaxFeSe}$ may be similar to the $T_c$ ($=31$ K) of $(\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}$, in which the Cs occupies the $2a$ site (0,0,0) (or on-center position) (Fig. 4(d))$^5$; our recent Rietveld refinement for XRD of $(\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}$ showed that the Cs atom occupied $2a$ and N atom in NH$_3$ occupied $4c$ site. Although the $c$ ($=14.145(8)$ Å) of the low-$T_c$ phase is much smaller than that ($=16.217(1)$ Å) of $(\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}$, the difference may be due to the different ionic radius and molecular orientation of NH$_3$. Consequently, we suggest that the site occupied by the Na atom may be different between the low-$T_c$ and high-$T_c$ phases, i.e., the former involves the on-center position (Fig. 4(c)), while the latter the off-center position (Fig. 4(b)). This change should be reasonable because of the limited number of sites allowed for Na. Namely, the maximum x allowed for Na in the on-center structure is 0.5, while that in the off-center structure is 1.5. Consequently, when increasing x, $(\text{NH}_3)_y\text{NaxFeSe}$ must take the off-center structure. This change probably leads to the different $c$'s that provide the different $T_c$'s.

Very recently, Guo et al. showed the presence of non-ammoniated $(\text{NH}_3$-free) $\text{Na}_x\text{Fe}_2\text{Se}_2$ ($T_c = 37$ K), $\text{NH}_3$-poor $\text{Na}_x\text{Fe}_2\text{Se}_2$ ($T_c = 45$ K) and $\text{NH}_3$-rich $\text{Na}_x\text{Fe}_2\text{Se}_2$ ($T_c = 42$ K)$^9$, and that Na in NH$_3$-free $\text{Na}_x\text{Fe}_2\text{Se}_2$ occupies the on-center position (called as ThCr$_2$Si$_2$ structure in Ref. 9). Although they did not report the x dependence of $T_c$ and c, it was suggested in their paper that the Coulomb repulsion of Na-Na is an origin for structural destabilization in $(\text{NH}_3)_y\text{M}_x\text{FeSe}$ crystals. We can easily predict that the off-center structure would be more destabilized because of smaller Na-Na distance (nearest Na-Na distance = a / 2) than that (nearest Na-Na distance = a) of the on-center structure. Nevertheless, because of the limited number of sites for Na, the on-center structure should change to the off-center structure. We suggest that the Coulomb repulsion may be reduced in the off-center structure if the Na atoms select the positions of the $4c$ and $2b$ sites to avoid approaching each other, which would realize the off-center structure in spite of the energetic disadvantage. However, this study still leaves the question open.

Table 1 lists the structural parameters and $T_c$ for the superconducting phases found in this study together with those reported by Guo et al.$^9$ As seen from Table 1, the c ($=14.257(7)$ Å) of the low-$T_c$ phase of $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$ prepared in this study is larger by ~0.6 Å than that ($=13.6678(4)$ Å) of the NH$_3$-free $\text{Na}_x\text{Fe}_2\text{Se}_2$($x' = 2x = 0.65$), which suggests that the low-$T_c$ phase contains NH$_3$ or coordinates between FeSe layers; our data listed in Table 1 correspond to those shown in Fig. 2(d). As described in the Results section, the value of y in $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$ was suggested to be 0.2–0.6 for the samples containing the low-$T_c$ phases, suggesting that the $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$ sample showing the $T_c$ of 32 K contains NH$_3$. The value is close to that, y = 0.3, for the ‘$\text{NH}_3$-poor’ phase exhibiting the high $T_c$ of 45 K in Guo’s

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**Figure 4.** Crystal structures determined for (a) $(\text{NH}_3)_y\text{Li}_x\text{FeSe}$ (ref. 2) and (d) $(\text{NH}_3)_y\text{Cs}_x\text{FeSe}$ (ref. 5), and the structure suggested for (b) high-$T_c$ phase and (c) low-$T_c$ phase of $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$. Green, brown, blue, yellow, and dark green balls refer to Se, Fe, Li, Na and Cs, respectively. Ball sizes reflect relative ionic radii. N and H are not shown. All schematic structures are drawn by ourselves based on the crystal structures determined for $(\text{NH}_3)_y\text{Li}_x\text{FeSe}$ (ref. 2) and $(\text{NH}_3)_y\text{Cs}_x\text{FeSe}$ (ref. 5), and those of high-$T_c$ and low-$T_c$ phases of $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$ are drawn by ourselves using atomic coordinates of $(\text{NH}_3)_y\text{Li}_x\text{FeSe}$ (ref. 2) and $(\text{NH}_3)_y\text{Cs}_x\text{FeSe}$ (ref. 5), respectively, and their lattice constants determined in this study.
Table 1. Structure and $T_c$ of superconducting phases found for (NH$_3$)$_y$Na$_x$FeSe. aTaken from this study. The data corresponds to Fig. 2(d). bTaken from ref. 9.

| composition                  | a (Å)    | c (Å)    | d (Å)    | $T_c$ (K) |
|-----------------------------|----------|----------|----------|-----------|
| low-$T_c$ phase             | (NH$_3$)$_y$Na$_{1.38(1)}$Fe$_{1.73(1)}$Se     | 3.889 (2) | 14.257 (7) | 7.12 32.5 |
| high-$T_c$ phase            | (NH$_3$)$_y$Na$_{1.10(1)}$Fe$_{2.10(1)}$Se     | 3.8266 (7) | 17.565 (9) | 8.78 46  |
| NH$_3$-free$^b$             | Na$_{0.80(1)}$Fe$_{1.86(1)}$Se                 | 3.7870 (4) | 13.6678 (4) | 6.83 37  |
| NH$_3$-poor$^b$             | (NH$_3$)$_{y}$Na$_{0.80(1)}$Fe$_{1.86(1)}$Se  | 3.7991 (2) | 17.4165 (4) | 8.71 45  |
| NH$_3$-rich$^b$             | —        | —        | —        | 11.1 42  |

It is significant that the occupancy of Li is fractional at $x < 1.5$ in (NH$_3$)$_y$Li$_x$FeSe (off-center structure), implying that the site occupancy may change continuously in the range $x = 0.1$ to 0.9. Therefore, the continuous variation of $c$ (Fig. 3(d)) may be due to this change of occupancy. In other words, changes in the presence and absence of Li at $4c$ and $2b$ sites may be what produce the continuous variation of $c$. In (NH$_3$)$_y$Li$_x$FeSe, the presence of some Li at these off-center positions is maintained through the $x$ range of 0.1 to 0.9, in contrast to the progression from on-center to off-center occupancy by Na in (NH$_3$)$_y$Na$_x$FeSe. This difference can be attributed to the different ionic radii of Na and Li.

A recent study reported $^{10}$ that the $T_c$ vs. $c$ plot of (NH$_3$)$_y$M$_x$FeSe showed saturated behavior, i.e., $T_c$ increases up to 45 K and then becomes saturated with a monotonic increase in $c$. However, the origin of this saturation behavior is different from that observed in (NH$_3$)$_y$Li$_x$FeSe (Fig. 3(b),(c)) because the $c$ does not increase monotonically against $x$ in (NH$_3$)$_y$Li$_x$FeSe. Here, we must ask the question why $c$ shows a maximum at $x = 0.5$, regardless of the simple prediction that an increase in the amount of Li would cause more expansion of FeSe plane spacing. The local structure around the Li atoms may change depending on $x$, i.e., the local structure around M (number of NH$_3$, molecular orientation…) may be different at different $x$’s. At the present stage, we note the possibility that the local structure best able to expand the plane-spacing is realized at $x = 0.5$, although no direct evidence has yet been obtained.

(NH$_3$)$_y$Na$_x$FeSe has more than two different superconducting phases (high-$T_c$ (or NH$_3$-poor) and low-$T_c$ phases in addition to NH$_3$-free and NH$_3$-rich phases$^9$), while (NH$_3$)$_y$Li$_x$FeSe has only a single phase with the high $T_c$. In addition, we recently found that (NH$_3$)$_y$Cs$_x$FeSe possessed only a single phase with low $T_c$ (not shown). This is because the Cs metal atom may not occupy off-center positions: the full occupation of those off-center positions would be difficult in view of the larger ionic radius of Cs. Thus, in this paper we conclude that metal occupation is the most significant key to determine the lattice constants and $T_c$. The influence of amount and molecular orientation of NH$_3$ should be further investigated. Detailed structural analysis of (NH$_3$)$_y$M$_x$FeSe using the Rietveld refinement of neutron diffraction results is necessary to confirm the exact structure of (NH$_3$)$_y$Na$_x$FeSe, which would make the effect of structure (occupation sites) on $T_c$ unequivocal.

Methods
Sample preparation and characterizations. The β-FeSe samples were prepared by the annealing method described in Ref. 6. The samples of (NH$_3$)$_y$M$_x$FeSe (M: Na and Li) were synthesized using the liquid NH$_3$ technique as described in Ref. 6. All the experimental procedures are the same as in our previous reports$^{5,6}$.

The DC magnetic susceptibility, $M / H$, of all samples was measured using a SQUID magnetometer (Quantum Design MPMS2); $M$ and $H$ refer to magnetization and applied magnetic field, respectively. The $M / H$ in this paper corresponds to mass magnetic susceptibility ($\text{cm}^3\text{g}^{-1} = \text{emu g}^{-1}$). The XRD patterns of the samples were measured with a Rigaku R-AXIS RAPID-NR X-ray diffractometer with Mo K$_\alpha$ source (wavelength $\lambda = 0.71078$ Å). The samples were introduced into quartz tubes in an Ar-filled glove box for $M / H$ measurements, while they were introduced into capillaries for XRD. The EDX was measured with an EDX spectrometer equipped with a scanning electron microscope (SEM) (KEYENCE VE-9800 - EDAX Genesis XM3).

The onset superconducting transition temperature ($T_{c-onset}$) of all pristine β-FeSe samples prepared in this study was 8.5 K, and the shielding fraction at 2.0 K was ~100%. The XRD patterns of all β-FeSe samples were consistent with each other, and the lattice constants, $a$ and $c$, of one β-FeSe sample were determined using LeBail refinement. The lattice constants, $a$ (3.77179(4) Å) and $c$ (5.5234(1) Å), of the sample were also consistent with published values$^{5,11,12}$. 

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Author Contributions
Y.K. (Okayama) designed this research project and supervised experiments. L.Z., X.M., Y.S., M.I. and S.N. synthesized (NH_3)_yM_xFeSe samples, and L.Z. and Y.S. characterized the samples prepared in this study by M/H, XRD and EDX. H.G. and E.U. joined the discussion of this study. The XRD measurement was assisted by Y.K. (Tokyo) and Y.I. Y.K. (Okayama) completed the paper under the discussion with L.Z. and H.G. Y.K. (Okayama) managed all parts of this paper.

Additional Information
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