Emergence of superconductivity in \((\text{NH}_3)_y\text{M}_x\text{MoSe}_2\) (\text{M}: \text{Li}, \text{Na} and \text{K})

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We report syntheses of new superconducting metal-doped MoSe$_2$ materials (M$_x$MoSe$_2$). The superconducting M$_x$MoSe$_2$ samples were prepared using a liquid NH$_3$ technique, and can be represented as \(\text{`(NH}_3)_y\text{M}_x\text{MoSe}_2\)\). The \(T_c\)s of these materials were approximately 5.0 K, independent of \(x\) and the specific metal atom. X-ray diffraction patterns of (NH$_3$)$_y$Na$_x$MoSe$_2$ were recorded using polycrystalline powders. An increase in lattice constant \(c\) showed that the Na atom was intercalated between MoSe$_2$ layers. The \(x\)-independence of \(c\) was observed in (NH$_3$)$_y$Na$_x$MoSe$_2$, indicating the formation of a stoichiometric compound in the entire \(x\) range, which is consistent with the \(x\)-independence of \(T_c\). A metallic edge of the Fermi level was observed in the photoemission spectrum at 30 K, demonstrating its metallic character in the normal state. Doping of MoSe$_2$ with Li and K also yielded superconductivity. Thus, MoSe$_2$ is a promising material for designing new superconductors, as are other transition metal dichalcogenides.

Searching for new superconducting materials is one of the most challenging and exciting areas of research. During the past decade, iron pnictides (FeAs) and chalcogenides (FeSe) have attracted much attention, not only from researchers interested in developing new superconductors, but also physicists who are interested in the mechanism of superconductivity$^{1-4}$. Recently, syntheses of metal-intercalated systems of FeSe using a liquid NH$_3$ technique have been extensively studied because various superconductors with high superconducting transition temperatures (\(T_c\)s) have been discovered$^{4-6}$; the highest \(T_c\)s are 46 K at ambient pressure$^1$ and 49 K at high pressure$^4$. The pressure-induced enhancement of \(T_c\) has also been confirmed for non-NH$_3$ K$_x$FeSe$^{10}$. Thus a layered compound like FeSe is a promising material platform for investigating high- \(T_c\) superconductors.

The Mo dichalcogenide family has also attracted much attention because of the emergence of its unique physical properties$^{11,12}$ and potential use in high-speed transistors$^{13,14}$. Electrostatic electron-doping of MoS$_2$ has produced superconductivity with a \(T_c\) as high as 10.8 K$^{11}$. The plot of \(T_c\) versus the accumulated two-dimensional (2D) electron density \(n_{\text{2D}}\) showed a dome-shaped curve, \(i.e.,\) the \(T_c\) was tuned by the extent of electrostatic electron-doping. The maximum \(T_c\) was 10.8 K at \(1.2 \times 10^{14}\text{ cm}^{-2}\). Also, a signature of 2D superconductivity was observed in electrostatically electron-accumulated MoS$_2$.$^{11}$ The chemical doping of MoS$_2$ with alkali and alkaline-earth metal atoms$^{15,16}$ provided superconductivity with \(T_c\)s lower than the maximum \(T_c\) of electrostatically electron-accumulated MoS$_2$. The chemical doping of MoS$_2$ was achieved using the liquid NH$_3$ technique, and many superconducting materials have been produced.

Very recently, electron-doping of MoSe$_2$ was achieved by the electrostatic method$^{17}$, and the \(T_c\) was precisely tuned in the same manner as in MoS$_2$. In the case of MoSe$_2$, only a Sr atom was intercalated, and MoSe$_2$ then showed a \(T_c\) as high as 5.0 K$^{13}$. This sample was prepared using the liquid NH$_3$ technique, and the chemical composition of Sr$_x$MoSe$_2$ can be expressed as \(\text{`(NH}_3)_y\text{Sr}_x\text{MoSe}_2\)\); where the nominal \(x\) was 0.2. The shielding fraction of (NH$_3$)$_y$Sr$_x$MoSe$_2$ was 60%.

Here, we report syntheses of M$_x$MoSe$_2$ samples (M: Li, K and Na) using the liquid NH$_3$ technique. In this study, Li, Na, K and Sr atoms were intercalated into MoSe$_2$ solids (only Sr-intercalation had previously been reported)$^{15}$.

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Single-crystal-like agglomerations of (NH\textsubscript{3})\textsubscript{y}M\textsubscript{x}MoSe\textsubscript{2} (M: Li, Na, K and Sr) were produced. Na-intercalation in (NH\textsubscript{3})\textsubscript{y}Na\textsubscript{0.5}MoSe\textsubscript{2} was indicated by its synchrotron powder X-ray diffraction (XRD) pattern. Energy dispersive X-ray spectroscopy (EDX) showed its chemical composition, and the amount of NH\textsubscript{3} was also determined from the mass difference before and after reaction. The superconducting parameters were determined from the magnetic field (H) dependence of magnetization (M). The photoemission spectrum at 30 K showed a clear edge on the Fermi level, indicating metallic behavior in the normal state.

Results

Crystal structure of (NH\textsubscript{3})\textsubscript{y}Na\textsubscript{0.5}MoSe\textsubscript{2}. Single crystals of pristine MoSe\textsubscript{2} were prepared using the annealing technique; details are described in the Methods section. A photograph of a pure MoSe\textsubscript{2} sample is shown in Figure S1a. A single-crystal structure analysis was produced using a piece of MoSe\textsubscript{2} (or single crystal) separated from a MoSe\textsubscript{2} agglomeration prepared in this study (Figure S1a); it is unclear whether an entire agglomeration is a single crystal or consists of multiple single crystals. A reasonable residual factor (R) could be obtained in this analysis (R = 2.4% and weighted R (wR) = 4.6%). Only one phase of MoSe\textsubscript{2} was included in the single crystal, and it was confirmed that no other phase such as Mo\textsubscript{3}Se\textsubscript{4} was included. The structure of the MoSe\textsubscript{2} single crystal was hexagonal (space group: No. 194, P6\textsubscript{3}2\textsubscript{1}mc). The lattice constants were \(a = 3.289(7) \text{ Å} \) and \(c = 12.96(3) \text{ Å} \), which are consistent with those \((a = 3.283 \text{ Å} \text{ and } c = 12.918 \text{ Å}\) reported previously for pristine MoSe\textsubscript{2}\textsuperscript{18}. Crystallographic data are listed in Table S1. As seen from the magnetic susceptibility \(M/H\) (emu g\textsuperscript{-1} cm\textsuperscript{3} g\textsuperscript{-1}) shown in Figure S2, no superconductivity was observed in any precursor MoSe\textsubscript{2} sample, implying no contamination with superconducting Mo\textsubscript{3}Se\textsubscript{4}. The chemical composition of one MoSe\textsubscript{2} agglomeration was determined to be ‘MoSe\textsubscript{2} (92)’ from the EDX spectrum (Figure S3). These analyses also show that the precursor material was not superconducting Mo\textsubscript{3}Se\textsubscript{4}, i.e., it was non-superconducting MoSe\textsubscript{2}. The EDX spectra, magnetic susceptibilities and single-crystal analyses guaranteed that all MoSe\textsubscript{2} agglomerations used for metal-intercalation throughout this study were in fact substantially ‘MoSe\textsubscript{2}’.

Metal-doped MoSe\textsubscript{2} samples were prepared using the liquid NH\textsubscript{3} technique. The experimental details are described in the Methods section. Here, it is worth noting that instead of a polycrystalline powder, in this study, a single-crystal or consists of multiple single crystals. A reasonable residual factor (\(R\)) could be obtained in this analysis (\(R = 3.289(7) \text{ Å} \) and \(c = 12.96(3) \text{ Å} \)) determined using high-quality (NH\textsubscript{3})\textsubscript{y}Na\textsubscript{0.5}MoSe\textsubscript{2} single crystals that yield sharp Bragg spots. This study is now in progress.

In this study, we tried to perform Rietveld refinement based on the model listed in Table S2 of Supplementary Information; the atomic coordinates listed in Table S2 were obtained by a structural analysis based on single-crystal X-ray data, but a reasonable \(R\) factor could not be obtained in the analysis because of the diffuse Bragg spots collected from the single crystal (Figure S1b). The complete Rietveld refinement could not be achieved using the above model, so it was not possible to determine the exact location of the Na atom. However,
the large expansion of \( c \) suggests that Na is located in the space between MoSe\(_2\) layers. If this is the case, the location of Na at a 2\( a \) site may be reasonable because of the presence of a large space around the 2\( a \) site. A possible crystal structure of (NH\(_3\))\( y \)Na\(_x\)MoSe\(_2\) is shown in Fig. 1c.

**Characterization of superconductivity in (NH\(_3\))\( y \)Na\(_x\)MoSe\(_2\).** Figure 2a shows the \( M/H \) – temperature (\( T \)) curves in zero field cooling (ZFC) and field-cooling (FC) modes for (NH\(_3\))\( y \)Na\(_{0.41(1)}\)MoSe\(_{2.04(1)}\). The \( T_c^{\text{onset}} \) and \( T_c \) were 6.0 and 5.0 K, respectively, for (NH\(_3\))\( y \)Na\(_{0.41(1)}\)MoSe\(_{2.04(1)}\): the \( T_c \) was determined from the crossing point of the extrapolation of the normal state and the drop of the \( M/H \) – \( T \) curve in ZFC mode, as seen from the inset in Fig. 2a. Here, it may be necessary to briefly comment on a small slow decrease in \( M/H \) below \( T_c^{\text{onset}} \) (Fig. 2a). The inhomogeneous Na-doping of MoSe\(_2\) may be suggested as its origin. However, as described later, the different \( x \) values in (NH\(_3\))\( y \)Na\(_x\)MoSe\(_2\) did not provide different \( T_c \) or \( T_c^{\text{onset}} \) values, which means that the inhomogeneous Na-doping cannot explain the slow decrease. The second possibility is that the (NH\(_3\))\( y \)Na\(_x\)MoSe\(_2\) agglomerations shown in Fig. 1a are not single crystals but aggregates of polycrystalline grains because the small size of superconducting grains often results in such a decrease. These possibilities are fully explored later.
The shielding fraction at 2.5 K was 100% for \((\text{NH}_3)_{0.4(1)}\text{Na}_{0.41(1)}\text{MoSe}_2.04(1)\); the shielding fraction was evaluated using the density \((\rho = 5.64 \text{ g cm}^{-3}\)) determined from the above chemical stoichiometry and lattice constants shown in the previous section. Here it should be noted that the above sample was made by Na-doping of an agglomeration of \(\text{MoSe}_2\). As a reference, the \(\text{M}/\text{H–T}\) plot of the \((\text{NH}_3)y\text{Na}_{0.5}\text{MoSe}_2\) sample prepared by Na-doping of polycrystalline \(\text{MoSe}_2\) powder is shown in Figure S5 of Supplementary Information. The \(T_c\) and \(T_{c\text{ onset}}\) (Figure S5) were the same as those (Fig. 2a) of a sample prepared by Na-doping of a \(\text{MoSe}_2\) agglomeration, but the shielding fraction was less than 1% at 2.5 K. The behavior of the \(\text{M}/\text{H–T}\) plot below \(T_c\text{ onset}\) (Figure S5) was also the same as that shown in Fig. 2a. These results may show that effective Na-doping can be performed on these agglomerations of \(\text{MoSe}_2\). Moreover, we suggest that the above small fraction (<1%) may originate in a limiting thickness of superconductivity, i.e., a thin superconducting area formed by metal-doping using polycrystalline \(\text{MoSe}_2\) powder. Therefore, throughout this paper, all studies were performed using the samples prepared by metal-doping of agglomerations of \(\text{MoSe}_2\).
Finally, we comment briefly on the Meissner fraction of \((\text{NH}_3)_y\text{Na}_{0.5}\text{MoSe}_2\) at 2.5 K (shielding fraction = 100% at 2.5 K (Fig. 2a)). The Meissner fraction was approximately 6.7% at 2.5 K which was evaluated from the \(M/H−T\) plot in FC mode (Fig. 2a), indicating a small size for superconducting grains. Therefore, this single-crystal like \((\text{NH}_3)_y\text{Na}_{0.41}\text{MoSe}_{2.04}\) may actually consist of polycrystalline superconducting grains, as previously suggested based on the slow drop observed in the \(M/H−T\) plot below \(T_{\text{onset}}\) (Fig. 2a). However, some of \((\text{NH}_3)_y\text{Na}_{0.5}\text{MoSe}_2\) samples showed a Meissner fraction of more than 20%. Figure S6 shows \(M/H−T\) plots of \((\text{NH}_3)_y\text{Na}_{0.5}\text{MoSe}_2\) exhibiting a Meissner fraction of 25%. Figure 2b shows the \(M−H\) curve at 2 K for \((\text{NH}_3)_y\text{Na}_{0.41}\text{MoSe}_{2.04}\) which exhibits a clear diamond-like shape. The lower critical field \(H_{c1}\) was determined to be 18 Oe from the expanded \(M−H\) curve (inset of Fig. 2b). It was concluded from the \(M−H\) curve (Fig. 2b) that the upper critical field, \(H_{c2}\), was >0.3 T, indicating a type-II superconductor. Figure S7 shows \(M/H−T\) plots at different \(H_s\) and the \(H−T\) phase diagram (Figure S7) was constructed from the \(T_{\text{onset}}\) at each \(H_s\); the fitted curve indicates the \(H_{c2}\) at each temperature. The positive curvature seen in Figure S7 is similar to the behavior of \((\text{NH}_3)_y\text{K}_{x}\text{MoS}_2\) reported recently. The \(H_{c2}\) at 0 K, \(H_{c2}(0)\), was evaluated to be 2.4 T. However, the data of the \(H_{c2}−T\) plot are confined near \(T_c\). Therefore, the \(H_{c2}\) is shown just for reference. We determined the London penetration depth, \(\lambda\), to be 520 nm, from \(H_{c2}\). The shape of the sample was assumed to be isotropic because the measurements of \(M−H−T\) at different \(H_s\) was performed using more than one agglomerations.

Figure 2c shows the \(x\) dependence of \(T_c\) in \((\text{NH}_3)_y\text{Na}_{x}\text{MoSe}_2\). The x value was determined from the EDX spectrum, and the \(x\) refers to the statistically averaged value with a small error bar falling within the range of the circle (Fig. 2c): the EDX was measured for several areas in one sample. The \(T_c\) was almost constant (~5 K) with an \(x\)-range of 0.4–1. The shielding fraction was higher than 35% in all samples. For the discussion, we plotted \(T_{\text{onset}}−x\) in Fig. 2c again because the previous reports on metal-doped \(\text{MoSe}_2\) and \(\text{MoSe}_2\) show the \(T_{\text{onset}}\). The \(T_{\text{onset}}\) was also constant (~6 K) in the \(x\)-range of 0.4–1. Therefore, we cannot point to an \(x\)-dependence of superconductivity in \((\text{NH}_3)_y\text{Na}_{x}\text{MoSe}_2\). Finally, we must comment that the maximum \(x\) is 1.0 in \((\text{NH}_3)_y\text{Na}_{x}\text{MoSe}_2\) if the Na occupies only a \(2\) \(a\) site in the \(6\) \(3\) \(m\) \(m\) lattice, as described in the subsequent section. To sum up, it must be stressed that the \(x\) range must be 0–1 in \((\text{NH}_3)_y\text{Na}_{x}\text{MoSe}_2\). A list of typical superconducting samples is shown in Table 1.

### Electronic structure of \((\text{NH}_3)_y\text{Na}_{x}\text{MoSe}_2\)

The photoemission spectrum of a single-crystal-like agglomeration of \((\text{NH}_3)_y\text{Na}_{x}\text{MoSe}_2\) measured at 30 K is shown in Fig. 3a; the spectrum was recorded at the \(\Gamma\) point using the Xe-\(\text{L}\) resonance line (8.44 eV). The photoemission intensity was observed on the Fermi level, \(i.e.,\) the metallic edge was clearly recorded. This shows that \(\text{Na}_{x}\text{MoSe}_2\) is metallic in the normal state, and the superconducting transition of \((\text{NH}_3)_y\text{Na}_{x}\text{MoSe}_2\) emerges from the metallic state. The evaluation of the superconducting gap in \((\text{NH}_3)_y\text{Na}_{x}\text{MoSe}_2\) has not yet been done due to the limited resolution of 15 meV in the photoelectron spectrometer, so this is future work. While the metallic edge was clearly observed in the normal state by Xe-\(\text{L}\) light, no signature of the metallic edge was obtained when changing Xe-\(\text{L}\) to the He-\(\text{L}\) resonance line (21.2 eV). We note that the surface of the \((\text{NH}_3)_y\text{Na}_{x}\text{MoSe}_2\) single crystal may be oxidized, as the photoemission spectrum using the Xe-\(\text{L}\) resonance line provides more bulk-sensitive results than He-\(\text{L}\). The successful observation of the metallic edge at the \(\Gamma\) point is fully treated in the Discussion section.

### Superconductivity in other metal-intercalated \(\text{MoSe}_2\)

Figure 3b,c show the \(M/H−T\) curves for \((\text{NH}_3)_y\text{Li}_{2}\text{MoSe}_2\) and \((\text{NH}_3)_y\text{K}_{3}\text{MoSe}_2\) in ZFC and FC modes. The \(T_{\text{onset}}\) and \(T_c\) were 6.5 and 5.0 K, respectively, for \((\text{NH}_3)_y\text{Li}_{2}\text{MoSe}_2\) and were 7.5 and 5.3 K for \((\text{NH}_3)_y\text{K}_{3}\text{MoSe}_2\). The shielding fraction at 2.5 K was 21% for \((\text{NH}_3)_y\text{Li}_{2}\text{MoSe}_2\), and 10.5% for \((\text{NH}_3)_y\text{K}_{3}\text{MoSe}_2\). These shielding fractions were roughly estimated using the \(\rho = (6.99 \text{ g cm}^{-3})\) of \(\text{MoSe}_2\) because the exact \(\rho\) could not be determined for \((\text{NH}_3)_y\text{Li}_{2}\text{MoSe}_2\) and \((\text{NH}_3)_y\text{K}_{3}\text{MoSe}_2\) owing to the absence of structural data (latticeconstants). Therefore, the values may be slightly overestimated, but the shielding fraction suggests that the superconducting phases can be formed by intercalating alkali metal atoms other than Na. The \(T_{\text{onset}}\)'s of these materials were higher than the 6 K of \((\text{NH}_3)_y\text{Na}_{x}\text{MoSe}_2\). However, the \(T_c\) was almost the same for three \((\text{NH}_3)_y\text{M}_{x}\text{MoSe}_2\)'s. Furthermore, we synthesized the superconducting \((\text{NH}_3)_y\text{Sr}_{x}\text{MoSe}_2\) (nominal \(x = 0.2\)), which showed a \(T_c\) \(T_{\text{onset}}\) as high as 4.8 K (7.0 K) \(M/H−T\) plots not.

| M   | \(x\) (nominal value) | \(T_c\) (K) | \(T_{\text{onset}}\) (K) | \(\rho_{\text{onset}}\) (Å) |
|-----|-----------------------|------------|-------------------------|-----------------------------|
| Na  | 0.3                   | 5.0        | 6.0                     | 1.02                        |
| Na  | 0.5                   | 4.8        | 6.0                     | 1.02                        |
| Na  | 0.5                   | 5.0        | 6.0                     | 1.02                        |
| Na  | 0.6                   | 4.7        | 6.0                     | 1.02                        |
| Na  | 0.6                   | 4.7        | 6.0                     | 1.02                        |
| Na  | 0.8                   | 5.0        | 6.0                     | 1.02                        |
| Na  | 0.8                   | 5.0        | 6.0                     | 1.02                        |
| Na  | 1.0                   | 4.7        | 6.0                     | 1.02                        |
| Li  | 0.5                   | 5.0        | 6.5                     | 0.76                        |
| K   | 0.5                   | 5.3        | 7.5                     | 1.38                        |
| Sr  | 0.2                   | 5.0        | 7.0                     | 1.18                        |

Table 1. List of representative samples prepared in this study.
shown); the \( T_c \) was the same as that reported previously\(^{15} \). The shielding fraction was \( \sim 2.5\% \) at 2.5 K which is lower than those of alkali-metal-doped MoSe\(_2\).

In the case of (NH\(_3\))\(_y\)M\(_x\)MoS\(_2\), the \( T_c \) onset generally increases with an increase in \( c \)\(^{15} \), and it increases with the ionic radius (\( r_{\text{ion}} \)) of the intercalant. However, the \( T_c \) onset of (NH\(_3\))\(_y\)Li\(_x\)MoSe\(_2\) deviates from this pattern\(^{15} \). The \( T_c \) onset vs. \( r_{\text{ion}} \) for (NH\(_3\))\(_y\)M\(_x\)MoSe\(_2\) (M: Li, Na, Sr and K) is plotted in Fig. 3d, together with that of (NH\(_3\))\(_y\)M\(_x\)MoS\(_2\) reported previously\(^{15,16} \).

Similar behavior is seen in the plots of \( T_c \) onset − \( r_{\text{ion}} \) of (NH\(_3\))\(_y\)M\(_x\)MoSe\(_2\) and (NH\(_3\))\(_y\)M\(_x\)MoS\(_2\). The \( T_c \) onset of (NH\(_3\))\(_y\)Li\(_x\)MoSe\(_2\) deviates from the suggested relationship, as does that of (NH\(_3\))\(_y\)Li\(_x\)MoS\(_2\)\(^{15} \). We briefly tried to synthesize (NH\(_3\))\(_y\)M\(_x\)MoSe\(_2\) (M: Rb, Cs, Ca, Ba, Sr and Yb) as well as (NH\(_3\))\(_y\)Li\(_{0.5}\)MoSe\(_2\), (NH\(_3\))\(_y\)Na\(_{0.5}\)MoSe\(_2\) and (NH\(_3\))\(_y\)K\(_{0.5}\)MoSe\(_2\). At the present stage, their superconductivity has not yet been observed, except for (NH\(_3\))\(_y\)Sr\(_x\)MoSe\(_2\) which was previously reported\(^{15} \).

**Discussion**

Very recently, Shi *et al.* succeeded in achieving superconductivity through electrostatic electron-doping of MoSe\(_2\)\(^{17} \). The maximum \( T_c \) of MoSe\(_2\) reaches 7.1 K at \( n_{2D} = 1.69 \times 10^{14} \text{ cm}^{-2} \), and the \( T_c \) can be tuned by the accumulated electron density. The maximum \( T_c \) is lower than the 10.8 K of MoS\(_2\)\(^{11} \) and the \( n_{2D} \) is higher than the 1.2 \( \times 10^{14} \text{ cm}^{-2} \) of MoS\(_2\)\(^{11} \). For MoSe\(_2\), a dome-like phase diagram of \( T_c \) vs. \( n_{2D} \) has not yet been observed because the number of metal-doped MoSe\(_2\) superconductors discovered is still small, i.e., a \( T_c \) in the \( n_{2D} \) range \(< 1.69 \times 10^{14} \text{ cm}^{-2} \), which will be achieved by chemical electron-doping, has not yet been plotted.

A fresh \( T_c - n_{2D} \) diagram (Fig. 4a) was prepared using the \( T_c - n_{2D} \) plot (electrostatic electron-doping) reported by Shi *et al.*\(^{17} \) and the \( T_c - n_{2D} \) plot (chemical electron-doping) for (NH\(_3\))\(_y\)MoSe\(_2\) samples produced in this study. Here, it should be noted that the 3D electron density, \( n_{3D} \) evaluated from the x and lattice volume in (NH\(_3\))\(_y\)Na\(_x\)MoSe\(_2\) was translated to 2D electron density \( n_{2D} \) by assuming the thickness of the channel region to be one layer (\( c/2 \)); the electron concentration donated from a metal atom to the MoSe\(_2\) layer was evaluated assuming that an alkali (alkali-earth) metal atom can donate only one (two) electron, i.e., complex processes such as back-electron transfer to NH\(_3\) were not considered. This is the same method used for the estimation of the \( T_c - n_{2D} \) plot for metal-doped MoS\(_2\)\(^{17} \). In the phase diagram, the \( T_c \)s of (NH\(_3\))\(_y\)Li\(_{0.5}\)MoSe\(_2\), (NH\(_3\))\(_y\)Na\(_{0.5}\)MoSe\(_2\) and (NH\(_3\))\(_y\)Sr\(_{0.261(1)}\)MoSe\(_2\) are also plotted for reference, although the x is an experimental nominal value except
The phase diagram of electron-accumulated MoSe₂ is shown in Figure 4a. This diagram is based on the \( T_c \)onset (diamonds) of (NH₃)ₓMₓMoSe₂ (this work) and those (circles) of electrostatically electron-accumulated MoSe₂ recently reported by Shi et al.\textsuperscript{17}. \( T_c \) is omitted in the formulas identifying differently M-intercalated (NH₃)ₓMₓMoSe₂. Figure 4b shows the expanded X-ray diffraction patterns (\( 2\theta = 4.0–8.0° \)) and Figure 4c shows the x-dependence of \( c \) for the three phases. The \( c \) values do not change with x.

As described in the Results section (Fig. 2c), no x-dependence of \( T_c \) or \( T_c \)onset was observed in (NH₃)ₓNaₓMoSe₂. Here, it is very interesting and significant to investigate whether the lattice constants \( (a,c) \) change with the x value in (NH₃)ₓNaₓMoSe₂. Figure 4b shows the expanded X-ray diffraction patterns (\( 2\theta = 4.0–8.0° \)), indicating that the 002 peaks due to doped and non-doped phases are observed at the constant \( 2\theta \) values.
although the peak intensity due to the doped phase increases monotonically with increasing x in the x-range of 0.35 to 0.86. From this result, it was found that the c does not change with x, suggesting that the stoichiometric 
(NH₃)ₓNaₓMoSe₂ is formed regardless of any increase in x. In other words, the chemical stoichiometry of 
(NH₃)ₓNaₓMoSe₂ does not change even when x increases, and only the fraction of the non-doped phase decreases.

Such behavior was recently observed in (NH₃)ₓKₓMoS₂, in which the KₓMoS₂ (2H structure) and KₓMoS₂ 
(1T and 1T' structure) are formed in low and high K concentrations, respectively. The constant Tc may be reasonably 
explained by the scenario that the stoichiometric (NH₃)ₓNaₓMoSe₂ compound (or the chemical compound 
with fixed x and y) is formed in the entire x range, i.e., the stoichiometric x value in (NH₃)ₓNaₓMoSe₂ does not change with increasing x as determined from EDX; the EDX estimates the x value including non-intercalated Na atoms. This scenario corresponds to the third possibility described in the Results section.

As seen from Fig. 4b, at higher x values than 0.7, a new peak was observed, indicating the presence of a new 
c-expanded phase. Figure 4c shows the x-dependence of c in (NH₃)ₓNaₓMoSe₂. From this graph, three different 
c values are found, due to (1) non-doped pure MoSe₂, (2) a Na-doped MoSe₂ phase, and (3) another Na-doped 
MoSe₂ phase with a larger MoSe₂ spacing. Since the Tc did not change in the entire x-range regardless of the 
formation of phase (3), it was unclear whether phase (3) is a new superconducting phase. To sum up, when 
x increases, two different Na-doped MoSe₂ phases with certain chemical stoichiometry seem to be formed in 
(NH₃)ₓNaₓMoSe₂. Further study is necessary to clarify the exact stoichiometry of their phases.

Finally, it is necessary to comment on the observation of a metallic edge on the Fermi level in the photoelectron 
spectrum measured at the Γ point. The band dispersion in bulk crystals of pure MoSe₂ shows an indirect 
band gap (Γ – (ΓK))², where (ΓK) means an intermediate state between Γ and K. However, the band dispersion 
in a single layer of MoSe₂ shows a direct band gap (K – K)². Therefore, a metallic edge for (NH₃)ₓNaₓMoSe₂ 
should be observed at the Γ point for MoSe₂ crystal. It was assumed that we are in a rigid-band picture of band dispersion. 
Furthermore, even if we assume a single-layer like MoSe₂, accompanied by expansion of the spacing between 
MoSe₂ layers due to Na-intercalation, a metallic edge must be observed at the K point. Therefore, a metallic edge should not be observed at the Γ point. Nevertheless, a metallic edge was clearly observed in the photoemission 
spectrum (Fig. 3a). Relevant to this question, it can be observed that the photoemission spectrum must detect all 
band dispersion of (NH₃)ₓNaₓMoSe₂ since the single crystal of MoSe₂ must be disordered to possess different 
crystal alignments. In other words, the photoemission spectrum of a polycrystalline-like (NH₃)ₓMₓMoSe₂ granule is recorded in Fig. 3a. This interpretation is reasonable since some disorder in the crystal is suggested by the XRD 
pattern shown in Fig. 1b.

Methods

Sample preparation and characterization. Single crystals of MoSe₂ were formed from a polycrystalline 
powder MoSe₂ sample by physical vapor transport using a furnace with different temperature zones; the powder 
MoSe₂ sample was prepared by annealing stoichiometric amounts of Mo and Se at 800 °C for 3 days and 1000 °C 
for 4 days, according to a procedure reported elsewhere. To form single crystals of MoSe₂, TeCl₄ was mixed with 
a MoSe₂ sample as a transport material, the powder MoSe₂ sample was set in the 1000 °C source area, and MoSe₂ 
single crystals were collected in the low-temperature zone at 900 °C. Here we have used the term ‘MoSe₂ single 
crystal’, but actually it is unclear whether the entirety of an agglomeration consists of one single crystal. Therefore, 
instead of the term ‘single crystal’, it may be valid to use the term ‘agglomeration of MoSe₂’.

The samples of (NH₃)ₓMₓMoSe₂ (M: Na, Li and K) were synthesized by the liquid NH₃ technique as follows: 
(1) stoichiometric amounts of Mo and Se, and an alkali metal were placed in a glass tube, and then NH₃ gas was condensed in the tube. (2) The metal dissolved in the liquid NH₃ at −60 °C, and the solution (colored 
blue) was kept below −50 °C for 6 days. (3) When the color disappeared, the NH₃ was removed by dynamical 
pumping at room temperature. The same method was used for Sr-intercalation in MoSe₂.

The DC magnetic susceptibility (M/H) of all samples was measured using a SQUID magnetometer (Quantum 
Design MPMS2). The single-crystal XRD patterns of the samples were measured using a Rigaku Saturn 724 dif-
fractometer with a Mo Kα source (wavelength λ = 0.71078 Å). The powder XRD patterns of (NH₃)ₓNaₓMoSe₂ 
and (NH₃)ₓNaₓMoSe₂ (x = 0 – 1) were obtained using synchrotron radiation (λ = 0.41371(1) Å) from the BL10XU 
beamline and (λ = 0.6887 Å) from the BL12B2 beamline, respectively, of the Spring-8 in Japan; the incident beam 
was focused by a stacked compound X-ray refractive lens. The samples were introduced into quartz tubes in an 
Ar-filled glove box for M/H measurements, or into capillaries for XRD; the quartz tubes were pumped and sealed 
under vacuum, while the capillaries were sealed under Ar atmosphere. The EDX was obtained with an EDX 
spectrometer equipped with a scanning electron microscope (SEM) (KEYENCE VE-9800-EDAX Genesis XM2), 
and the photoemission spectrum with a SCIENTAOMICRON R4000 analyzer and a discharge lamp (SPECs). 
The Fermi level of the sample was referenced to that of gold, which was in electrical contact with the sample. 
The sample was cleaved in the ultrahigh-vacuum chamber for the measurement of photoemission spectrum. 
The photoemission spectrum was measured in an ultrahigh vacuum of ~5 × 10⁻⁹ Pa.

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Author Contributions
Y.K. designed this research project and supervised experiments. X.M., S.N. and L.Z. synthesized and characterized MoSe₂ and (NH₃)yMxMoSe₂ samples. H.T.L.N., T.K. (Osaka Univ.), N.H., Y.O., H.I. and Y.-F.L. measured the powder XRD pattern at Spring-8. X.M. and L.Z. analyzed powder XRD data. H.O. measured and analyzed the single-crystal XRD data. K.T. and T.Y. measured photoemission spectra at low temperatures. Y.K. prepared the paper with the help of X.M., H.G., R.E., T.K. (Okayama Univ.) and T.Y.

Additional Information
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