Correlation of superconductivity with crystal structure in \((\text{NH}_3)_y\text{Cs}_x\text{FeSe}\)

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The superconducting transition temperature \(T_c\) of ammoniated metal-doped FeSe \((\text{NH}_3)_yM_{1-x}\text{FeSe}\) (\(M\): metal atom) has been scaled with the FeSe plane spacing, and it has been suggested that the FeSe plane spacing depends on the location of metal atoms in \((\text{NH}_3)_yM_x\text{FeSe}\) crystals. Although the crystal structure of \((\text{NH}_3)_y\text{Li}_x\text{FeSe}\) exhibiting a high \(T_c\) (~44 K) was determined from neutron diffraction, the structure of \((\text{NH}_3)_yM_x\text{FeSe}\) exhibiting a low \(T_c\) (~32 K) has not been determined thus far. Here, we determined the crystal structure of \((\text{NH}_3)_y\text{Cs}_{0.4}\text{FeSe}\) \((T_c = 33 \text{ K})\) through the Rietveld refinement of the x-ray diffraction (XRD) pattern measured with synchrotron radiation at 30 K. The XRD pattern was analyzed on two different models, on-center and off-center, under a space group of 14/mmm. In the on-center structure, the Cs occupies the 2\(a\) site and the N of \(\text{NH}_3\) may occupy either the 4\(c\) or 2\(b\) site, or both. In the off-center structure, the Cs may occupy either the 4\(c\) or 2\(b\) site, or both, while the N occupies the 2\(a\) site. Only an on-center structure model in which the Cs occupies the 2\(a\) and the N of \(\text{NH}_3\) occupies the 4\(c\) site provided reasonable results in the Rietveld analysis. Consequently, we concluded that \((\text{NH}_3)_y\text{Cs}_{0.4}\text{FeSe}\) can be assigned to the on-center structure, which produces a smaller FeSe plane spacing leading to the lower \(T_c\).

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I. INTRODUCTION

The study on metal-doped FeSe is one of the most exciting research subjects because its superconducting transition temperature \((T_c)\) has reached a value greater than 45 K [1–4]. Metal-doped FeSe materials can be synthesized using the high-temperature-annealing method [1,5–8] and liquid-ammonia technique [2,3,9–14], and its \(T_c\) can be increased by increasing the FeSe plane spacing [2,4]. On the other hand, it was found that pressure application resulted in a high-\(T_c\) phase with the \(T_c\) reaching a value greater than 45 K [1,2]. Currently, the highest \(T_c\) reported in bulk superconductors of metal-doped FeSe is 49 K at 21 GPa [2]. Even at ambient pressure, the \(T_c\) of ammoniated metal-doped FeSe materials has reached 46 K for \((\text{NH}_3)_y\text{Na}_{0.5}\text{FeSe}\) [3]. The insertion of \(\text{NH}_3\) molecules or ammoniated metal coordinates between the FeSe layers in metal-doped FeSe can increase the FeSe plane spacing to produce a higher \(T_c\). From the analogy with the relation between the \(T_c\) and interlayer distance in ZrNCl [15] and HfNCl [16], we believe that increasing the lattice constant \(c\) (or FeSe plane spacing) increases two-dimensionality (2D) to improve Fermi-surface nesting, which enhances spin fluctuation to reinforce the superconducting pairing interaction [2].

Here, it is important to note that the ionic radius of the metal atom inversely correlates with the \(T_c\) [11] because metal atoms such as Rb and Cs with larger ionic radii lead to a smaller FeSe plane spacing and, in turn, lower \(T_c\). Our studies on the relationship between \(c\) and \(T_c\) in \((\text{NH}_3)_yM_x\text{FeSe}\) clarified that the \(T_c\) could be directly scaled with the FeSe plane spacing [2,11]. Therefore, we must investigate the reason why the metal atoms with smaller ionic radius can produce higher FeSe plane spacing. Our previous study on \((\text{NH}_3)_y\text{Na}_x\text{FeSe}\) exhibiting different \(T_c\)’s, 32 and 46 K [3,12,17], suggested that a difference in the location of metal atoms in each phase resulted in a different FeSe plane spacing, leading to a different \(T_c\). This was suggested from the analogy of the FeSe plane spacing and \(T_c\) of the high-\(T_c\) \((T_c = 46 \text{ K})\) phase in \((\text{NH}_3)_y\text{Na}_x\text{FeSe}\) with those of \((\text{NH}_3)_y\text{Li}_x\text{FeSe}\) \((T_c = 44 \text{ K})\) [3,10], while the FeSe plane spacing and \(T_c\) of the low-\(T_c\) phase \((T_c = 32 \text{ K})\) [12,17] with those of \(\text{K}_x\text{FeSe}\) \((T_c = 31 \text{ K})\) [5]. The Rietveld refinement of the neutron diffraction of \((\text{NH}_3)_y\text{Li}_x\text{FeSe}\) clarified that the Li occupied the 4\(c\) and 2\(b\) sites and the N of \(\text{NH}_3\) occupied the 2\(a\) site provided reasonable results in the Rietveld analysis. Consequently, we concluded that \((\text{NH}_3)_y\text{Cs}_{0.4}\text{FeSe}\) can be assigned to the on-center structure, which produces a smaller FeSe plane spacing leading to the lower \(T_c\).
and the N of NH$_3$ occupied the 4c site. The chemical composition was determined to be (NH$_3$)$_{0.79(4)}$Cs$_{0.26(4)}$FeSe. In the analysis, a deficiency of Fe was not observed. Furthermore, we investigated the $x$ dependence of $T_c$ in (NH$_3$)$_x$Cs$_y$FeSe and discussed the constant $T_c$ value observed from view of the structure.

II. EXPERIMENTAL

The β-FeSe sample was prepared using the annealing method described in Ref. [11]. The sample of (NH$_3$)$_x$Cs$_y$FeSe was synthesized using the liquid-NH$_3$ technique described in Ref. [11] with a nominal $x = 0.4$. The experimental procedure is the same as that in our previous reports [2,11]. The dc magnetic susceptibilities $M/H$'s, of all samples were measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS2); here, $M$ and $H$ refer to the magnetization and applied magnetic field, respectively. The $M/H$ in this paper corresponds to the mass magnetic susceptibility (cm$^3$ g$^{-1}$ = emu g$^{-1}$). The XRD pattern of the sample was measured with synchrotron radiation (wavelength $\lambda = 0.400176(2)$ Å) in BL02B2 of SPring-8, Japan. The sample was introduced into a quartz tube and a capillary for Ar-filled glove box (H$_2$O, O$_2$ < 0.1 ppm); the capillary was filled with He gas. Le Bail and Rietveld refinements were performed using the GSAS program.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the temperature dependence of magnetic susceptibility ($M/H$ in cm$^3$ g$^{-1}$) at zero-field cooling (ZFC) and field cooling (FC) for the (NH$_3$)$_x$Cs$_y$FeSe sample. The onset superconducting transition temperature ($T_c$onset) and $T_c$ were determined to be 35 and 33.5 K, respectively, from the $M/H - T$ plots. As shown in the inset of Fig. 1(a), the $T_c$ is determined from the cross point of the drop of $M/H$ and the extrapolation of the normal state. The shielding fraction of the sample was 25% at 10 K. The $M/H - T$ plots suggest the presence of pure β-FeSe, which exhibits a $T_c$ as high as 8 K.

Figure 1(b) shows the XRD patterns measured at different temperatures. These patterns suggest that the crystal structure is the same in the entire temperature range, i.e., no structural phase transition occurs. The Le Bail fitting of the XRD pattern at 30 K is shown in Fig. 1(c). The Le Bail fitting was achieved assuming the presence of three different crystal phases: (NH$_3$)$_x$Cs$_y$FeSe, β-FeSe, and α-FeSe. The XRD pattern consists of the overlapped peaks from three phases, but some peaks can be assigned to only a single phase among three phases, indicating the presence of three phases. Thus,

![Fig. 1. (a) $M/H$ versus $T$ plots and (b) temperature-dependent XRD patterns of (NH$_3$)$_x$Cs$_y$FeSe. In (b), the peaks due to only a single phase among three phases of (NH$_3$)$_x$Cs$_y$FeSe, β-FeSe, and α-FeSe are shown by symbols +, #, and *, respectively. (c) Le Bail fitting curve (red line) and experimental XRD pattern (x mark) of (NH$_3$)$_x$Cs$_y$FeSe at 30 K. Ticks indicate the positions of Bragg reflections predicted from the lattice constants suggested for (NH$_3$)$_x$Cs$_y$FeSe (top), β-FeSe (middle), and α-FeSe (bottom). The difference between the Le Bail fitting and experimental XRD is indicated in blue. (d) Lattice constants $a$ and $c$ are plotted as a function of $T$.](104508-2)
We determined the lattice constants for these crystal phases based on previous reports; the space groups for (NH₃)₂Cs, FeSe, β-FeSe, and α-FeSe were I4/mmm (#139) [5,10,11,14], P4/mmm (#129) [11,18,19], and P6₃/mmc (#194) [11,20], respectively. The lattice constants a and c were determined to be 3.8082(2) and 16.097(1) Å, respectively, for (NH₃)₂Cs, FeSe. The lattice constants of three phases were refined together with background and peak-shape (profile-function) parameters; CWF profile function 2 of the GSAS program was used for the profile function. This function employs a multiterm Simpson’s rule integration of the pseudo-Voigt function [21]. The parameters of profile functions are refined independently for each phase.

In the refinement with the off-center model described above, the fractions of (NH₃)₂Cs, FeSe, β-FeSe, and α-FeSe were evaluated to be 37, 33, and 30%, respectively. The a and c of (NH₃)₂Cs, FeSe were determined to be 3.8050(3) and 16.0666(2) Å, respectively, which are almost the same as those, 3.8082(2) and 16.097(1) Å, evaluated from the Le Bail fitting [Fig. 1(c)]. However, the B of the Cs at the 4c site rapidly increased to 63(12) Å², while the B of the Cs at the 2b site had a negative value. Furthermore, the occupancy of N diverged. As a reference, the XRD pattern calculated based on the off-center structure of the (NH₃)₂Cs, FeSe phase and the structures of β-FeSe and α-FeSe is shown in Fig. 3(a), together with the experimental XRD pattern; the weighted R factor (wR_pe) and pattern R factor (R_p) were 11.3 and 7.7%, respectively. From the unreasonable B factors and occupancy, we must conclude that this refinement is not successful, showing that the off-center model cannot be applied for the (NH₃)₂Cs, FeSe phase. The logarithmic scale of the experimental XRD pattern is shown together with the logarithmic-scaled pattern calculated (off-center model) in Fig. 3(b), to clearly show the entire XRD pattern.

As shown in Fig. 2, we subsequently analyzed the XRD pattern based on the on-center model (space group: I4/mmm) for (NH₃)₂Cs, FeSe. In the same manner as the analysis based on the off-center model for (NH₃)₂Cs, FeSe, β-FeSe and α-FeSe were included in the analysis. The structures of β-FeSe and α-FeSe are the same as those used in the off-center structure analysis. The lattice constants of three phases were refined together with the background, and the parameters of the profile function were independently refined for each phase; the profile function is the same as that in the off-center model.

In the (NH₃)₂Cs, FeSe phase, the Cs atom was located at the 2a (0, 0, 0) site, while the N atom of NH₃ was located at the 2b (0, 0, 1/2) site. The occupancy of Cs and N were refined, while the occupancy of Fe and Se were fixed to 1.0. The Debye-Waller factor B (B = 8π²U, U: isotropic thermal-displacement of atom) for all atoms (Fe, Se, Cs, and N) were refined in the (NH₃)₂Cs, FeSe phase, and z at the 4e site (Se) were refined. The refinements of β-FeSe and α-FeSe were performed together with that of (NH₃)₂Cs, FeSe. In β-FeSe, the Fe and Se atoms were located at 2a (3/4, 1/4, 0) and 2c (1/4, 1/4, z) sites (choice #2 of P4/mmm), respectively, and the z at the 2c site and B values at both sites were refined; occupancies at both sites were fixed to 1.0. In α-FeSe, the Fe and Se atoms were located at the 2a (0, 0, 0) and 2c (1/3, 2/3, 1/4) sites, respectively, and the B values at both sites were refined. The lattice constants of three phases were refined together with background and peak-shape (profile-function) parameters; CWF profile function 2 of the GSAS program was used for the profile function. This function employs a multiterm Simpson’s rule integration of the pseudo-Voigt function [21]. The parameters of profile functions are refined independently for each phase.

Next, we discuss the Rietveld analysis of the off-center structure of the (NH₃)₂Cs, FeSe phase, the Cs atom was located at the 4d (0, 1/2, 0) and 2e (0, 0, 1/2) sites, and the N of NH₃ was located at the 2a site (0, 0, 0); the structure is the same as that of (NH₃)₂Li, FeSe [10]. The H atom was not included in the analysis throughout this study. The occupancy of Cs and N were refined, while the occupancy of Fe and Se were fixed to 1.0. The Debye-Waller factor B (B = 8π²U, U: isotropic thermal-displacement of atom) for all atoms (Fe, Se, Cs, and N) were refined in the (NH₃)₂Cs, FeSe phase, and z at the 4e site (Se) were refined. The refinements of β-FeSe and α-FeSe were performed together with that of (NH₃)₂Cs, FeSe. In β-FeSe, the Fe and Se atoms were located at 2a (3/4, 1/4, 0) and 2c (1/4, 1/4, z) sites (choice #2 of P4/mmm), respectively, and the z at the 2c site and B values at both sites were refined; occupancies at both sites were fixed to 1.0. In α-FeSe, the Fe and Se atoms were located at the 2a (0, 0, 0) and 2c (1/3, 2/3, 1/4) sites, respectively, and the B values at both sites were refined. The lattice constants of three phases were refined together with background and peak-shape (profile-function) parameters; CWF profile function 2 of the GSAS program was used for the profile function. This function employs a multiterm Simpson’s rule integration of the pseudo-Voigt function [21]. The parameters of profile functions are refined independently for each phase.

As shown in Fig. 2, we subsequently analyzed the XRD pattern based on the on-center model (space group: I4/mmm) for (NH₃)₂Cs, FeSe. In the same manner as the analysis based on the off-center model for (NH₃)₂Cs, FeSe, β-FeSe and α-FeSe were included in the analysis. The structures of β-FeSe and α-FeSe are the same as those used in the off-center structure analysis. The lattice constants of three phases were refined together with the background, and the parameters of the profile function were independently refined for each phase; the profile function is the same as that in the off-center model.

In the (NH₃)₂Cs, FeSe phase, the Cs atom was located at the 2a (0, 0, 0) site, while the N atom of NH₃ was located at the 2b (0, 0, 1/2) site. The occupancy of Cs and N were refined, while the occupancy of Fe and Se were fixed to 1.0. The B values for all elements and z at the 4e site were refined in the (NH₃)₂Cs, FeSe phase. The Rietveld refinement showed a negative occupancy and negative B for the N atom (2b site), indicating that this structure (on-center model) can also be ruled out for the (NH₃)₂Cs, FeSe phase.
Next, in the on-center model, the N atom was moved to the 4c (0, 1/2, 0) site from the 2b site. The occupancy of Cs and N, B values of all elements, and z of the 4e site were refined in this analysis. This analysis successfully provided reasonable values for occupancy, B, and z, as listed in Table I. The a and c for (NH₃),Cs,FeSe were 3.8075(2) and 16.048(2) Å, respectively, which are the same as those [3.8082(2) and 16.097(1) Å] at 30 K obtained using Le Bail fitting [Fig. 1(d)]. The refined structures of β-FeSe and α-FeSe are also reasonable (see Table I). Consequently, the on-center structure in which the Cs occupies the 2a site and the N occupies the 4c site was identified for (NH₃),Cs,FeSe. From the determined occupancies of N and Cs, the chemical stoichiometry was evaluated to be (NH₃)₀.37(4)Cs₀.268(4)FeSe. The x value [0.268(4)] determined from the occupancy of Cs at the 2a site was consistent with that [x = 0.255(5)] reported previously for the other batch of (NH₃),Cs,FeSe (nominal x = 0.4) [11] and was almost consistent with the nominal x value (=0.4), indicating a reliable occupancy. However, it should be recognized that the occupancy is evaluated under the restriction of I4/mmm symmetry.

The fractions of (NH₃),Cs,FeSe, β-FeSe, and α-FeSe were 36, 34, and 32%, respectively. The wR and R were 10.7 and 7.1%, respectively, indicating a better analysis with the on-center model than the off-center model. The calculated XRD pattern is shown in Fig. 3(c), together with the experimental XRD pattern, and the logarithmic scale of the experimental XRD pattern is shown together with the calculated pattern in Fig. 3(d), to clearly show the entire experimental and calculated XRD patterns.

To confirm the on-center structure (Cs: 2a site, N: 4c site), the N atom was assumed at both the 2b and 4c sites, and refinement was performed. Consequently, the occupancy for the N at the 2b site vanished, and that for the N at the 4c site had the same value as that in the analysis based on the on-center model (Cs: 2a site, N: 4c site) described above. The B values of N at the 2b and 4c sites provided negative and reasonable values, respectively. These results imply that the N does not exist at the 2b site; rather, it exists at the 4c site. Thus, our analysis of the XRD pattern of the (NH₃),Cs,FeSe sample successfully resulted in the on-center structure (Cs: 2a site, N: 4c site) for the (NH₃),Cs,FeSe sample.

FIG. 3. Curves (red line) calculated using the Rietveld refinement and the experimental XRD pattern (x mark) of (NH₃),Cs₀.4FeSe at 30 K. Rietveld refinement was achieved based on (a) the off-center model and (c) the on-center model. Ticks indicate the positions of Bragg reflections predicted from the lattice constants suggested for (NH₃),Cs₀.4FeSe (top), β-FeSe (middle), and α-FeSe (bottom). The difference between the calculated and experimental XRD patterns is indicated in blue. In the inset of (a) and (c), the calculated and experimental XRD pattern (expanded) in high 2θ angle is shown. The logarithmic scale of the experimental XRD pattern and the logarithmic-scaled pattern calculated using (b) the off-center and (d) the on-center models.
TABLE I. Final crystal structure of (NH₃)ₓCs₀.₄FeSe determined using Rietveld refinement.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure Type</th>
<th>Lattice Constant</th>
<th>Occupancy</th>
<th>B (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>Body-centered tetragonal lattice: I4/mmm (No. 139)</td>
<td>a = 3.8075(2) Å, c = 16.048(2) Å</td>
<td>1.0 0.00000 0.50000 0.25000 0.2(1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2a Fe 1.0 0.75000 0.25000 0.00000 1.2(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2c Se 1.0 0.00000 0.00000 0.00000 1.4(2)</td>
<td></td>
</tr>
<tr>
<td>2)</td>
<td>Tetragonal lattice: P4/mmm (No. 129, choice 2)</td>
<td>a = 3.7666(8), c = 5.458(2) Å</td>
<td>0.5 0.25000 0.50000 0.00000 1.4(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2a Fe 1.0 0.75000 0.25000 0.00000 1.2(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2c Se 1.0 0.00000 0.00000 0.00000 1.4(2)</td>
<td></td>
</tr>
<tr>
<td>3)</td>
<td>Hexagonal structure: P6₃/mmc (No. 194)</td>
<td>a = 3.6166(3), c = 5.9293(8) Å</td>
<td>0.5 0.37500 0.50000 0.00000 1.4(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2a Fe 1.0 0.75000 0.25000 0.00000 1.2(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2c Se 1.0 0.00000 0.00000 0.00000 1.4(2)</td>
<td></td>
</tr>
</tbody>
</table>

The structure suggested for (NH₃)ₓCsₓFeSe is shown in Fig. 4(a). Here, we must comment that the fraction of 36% determined from the Rietveld refinement is a little different from the stoichiometry of (NH₃)₀.₃₇x(Cs₁.₆₈xFe₂.₈₁x)Se. This implies the absence of a deficiency of Fe in (NH₃)ₓCsₓFeSe, which is reasonable from the low paramagnetic susceptibility observed in the normal state [Fig. 1(a)]. Finally, we calculated the difference Fourier map using the on-center model structure (Cs: 2a site, N: 4c site), which refers to electron density distribution evaluated from the difference between the XRD observed and that calculated with the on-center model. No electron densities were observed at the 2a and 4c sites, showing clearly that the above on-center model is reasonable. In addition, the electron density was observed at the 2a site in the difference Fourier map when the N atom was located at the 2a site (off-center model), indicating the electrons are inefficient, i.e., the element is not N but Cs at 2a site. This supports the validity of the on-center model.

We attempted to determine the occupancy of Fe in the (NH₃)ₓCsₓFeSe phase. In the final structure [Table I and Fig. 4(a)], only the occupancy and B of Fe (4d site) were refined to determine the deficiency of Fe, providing the chemical phase. The structure suggested for (NH₃)ₓCsₓFeSe is shown in Fig. 4(a). Here, we must comment that the fraction of 36% determined from the Rietveld refinement is a little different from the shielding fraction (~25%) from the magnetic susceptibility. Such a deviation is also found in the previous report [11]. One possibility for the lower volume fraction (~25%) determined from magnetic susceptibility is that the presence of nonsuperconducting/magnetic α-FeSe may suppress the superconducting state. At the present stage, the origin remains to be clarified.

We attempted to determine the occupancy of Fe in the (NH₃)ₓCsₓFeSe phase. In the final structure [Table I and Fig. 4(a)], only the occupancy and B of Fe (4d site) were refined to determine the deficiency of Fe, providing the chemical...
TABLE II. Selected interatomic distances and angles in the off-center and on-center models for (NH₃)ₓCsₓFeSe and those in (NH₃)ₓLiₓFeSe (off-center structure) and KₓFeSe (on-center structure). The site where each element occupies is also shown.

<table>
<thead>
<tr>
<th></th>
<th>Off-center model</th>
<th>On-center model</th>
<th>(NH₃)ₓLiₓFeSeᵃ</th>
<th>KₓFeSeᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Se (Å)</td>
<td>2.4074(2)</td>
<td>2.4229(1)</td>
<td>2.408(1)</td>
<td>2.440(4)</td>
</tr>
<tr>
<td>4d-4e</td>
<td>4d-4e</td>
<td>4d-4e</td>
<td>4d-4e</td>
<td></td>
</tr>
<tr>
<td>Se-Fe-Se (Å)</td>
<td>104.4217(1)</td>
<td>103.5818(1)</td>
<td>104.40(8)</td>
<td>106.60(4)</td>
</tr>
<tr>
<td>4d-4e-4d</td>
<td>4d-4e-4d</td>
<td>4d-4e-4d</td>
<td>4d-4e-4d</td>
<td></td>
</tr>
<tr>
<td>M-N (Å)</td>
<td>1.9025(1)</td>
<td>1.9038(1)</td>
<td>1.9029(1)</td>
<td>No</td>
</tr>
<tr>
<td>2a-4c</td>
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<td>2a-4c</td>
<td></td>
</tr>
<tr>
<td>M-N (Å)</td>
<td>2.6905(1)</td>
<td>No</td>
<td>2.6912(1)</td>
<td>No</td>
</tr>
<tr>
<td>2b-2a</td>
<td>2b-2a</td>
<td>2b-2a</td>
<td>2b-2a</td>
<td></td>
</tr>
<tr>
<td>N-Se (Å)</td>
<td>3.7010(3)</td>
<td>3.1523(3)</td>
<td>3.7207(1)</td>
<td>No</td>
</tr>
<tr>
<td>2a-4e</td>
<td>2a-4e</td>
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<td>2a-4e</td>
<td></td>
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<tr>
<td>M-Se (Å)</td>
<td>3.1746(3)</td>
<td>3.6828(2)</td>
<td>3.1972(1)</td>
<td>3.4443(4)</td>
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<tr>
<td>4c-4e</td>
<td>2a-4e</td>
<td>4c-4e</td>
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<tr>
<td>M-Se (Å)</td>
<td>2.5414(4)</td>
<td>No</td>
<td>2.5693(1)</td>
<td>No</td>
</tr>
<tr>
<td>2b-4e</td>
<td>2b-4e</td>
<td>2b-4e</td>
<td>2b-4e</td>
<td></td>
</tr>
</tbody>
</table>

ᵃTaken from Ref. [10].
ᵇTaken from Ref. [5].

off-center structures. Actually, depending on the ionic radius, the structure adopted seems to be different. Our recent paper showed that (NH₃)ₓNaₓFeSe has two superconducting phases (Tc = 32 K and 46 K [17]) depending on the x value, and the phases have different c values [14.145(8) Å for the 32 K phase and 17.565(7) Å for the 46 K phase].

When varying the nominal x value from 0.0 to 1.3 [Fig. 4(b)], and it was constant at 33 ± 2 K. This indicates that only an on-center structure is adopted in (NH₃)ₓCsₓFeSe, while the high-Tc phase (Tc ∼ 33 K) was realized in (NH₃)ₓCsₓFeSe, which is different from (NH₃)ₓNaₓFeSe and (NH₃)ₓLiₓFeSe, indicating the ionic radius of the intercalant is a key for determining the Tc, i.e., the larger ionic radius leads to the lower Tc.

IV. CONCLUSIONS

The Rietveld refinement of the XRD pattern of (NH₃)ₓCsₓFeSe was successfully achieved, and it revealed an on-center structure in which the Cs and the N of NH₃ occupy the 2a and 4c sites, respectively. This suggests that the low-Tc phase (Tc ∼ 32 K) found in (NH₃)ₓMₓFeSe takes the on-center structure, while the high-Tc phase (Tc ∼ 45 K) takes the off-center structure, as determined for (NH₃)ₓLiₓFeSe [10]. The on-center structure has a smaller FeSe plane spacing than that of the off-center structure, and the FeSe plane spacing closely relates to the Tc. This paper clarified not only the structural difference between the low-Tc and high-Tc phases in (NH₃)ₓMₓFeSe, but also the effect of the location of the metal and NH₃ atoms on the FeSe plane spacing (or Tc). As the location of metal atoms with relatively large and small ionic radii (Cs and Li) was determined, the next target for determination must be FeSe materials incorporating a metal atom with intermediate ionic radius such as Na, which produces multiple superconducting phases (high-Tc and low-Tc phases [12,17]). This paper constitutes a step towards clarifying the correlation between the crystal structure and Tc in (NH₃)ₓMₓFeSe.

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