New ethylenediamine-intercalated superconductor 
\((\text{C}_2\text{H}_8\text{N}_2)_y\text{Ta}_2\text{PdSe}_6\) with \(T_c = 4.5\) K

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Abstract. A new superconductor \((\text{C}_2\text{H}_8\text{N}_2)_y\text{Ta}_2\text{PdSe}_6\) with \(T_c = 4.5\) K has successfully been synthesized via the intercalation of ethylenediamine (EDA) into \(\text{Ta}_2\text{PdSe}_6\). It has been found that the co-intercalation of lithium suppresses the superconductivity in \((\text{C}_2\text{H}_8\text{N}_2)_y\text{Ta}_2\text{PdSe}_6\), indicating that the electron doping is harmful to the superconductivity. The origin of the appearance of superconductivity via the intercalation of only EDA into \(\text{Ta}_2\text{PdSe}_6\) has been discussed.

1. Introduction

Superconductors including 4\(d\) and 5\(d\) transition metals such as \(\text{T}_2\text{Pd}_x\text{Ch}_5\) (\(\text{T} = \text{Nb, Ta} ; \text{Ch} = \text{S, Se}\)) have attracted attention owing to their extremely high upper critical fields \(H_{c2}'s\), which are caused by the strong spin-orbit interaction [1-4]. The layered compound \(\text{Ta}_2\text{PdSe}_6\) is not a superconductor but a degenerate semiconductor or a semimetal, though its crystal structure is analogous to that of \(\text{T}_2\text{Pd}_x\text{Ch}_5\), as shown in Fig. 1(a) [5]. Recently, it has also attracted great attention that the superconducting transition temperature \(T_c\) of the layered superconductor \(\text{FeSe}\) dramatically increases from 8 K to ~ 45 K via the co-intercalation of alkali metal or alkali earth metal and ammonia or organic molecules [6-14]. Since \(\text{Ta}_2\text{PdSe}_6\) has double Se layers weakly combined with the van der Waals force as well as \(\text{FeSe}\), the appearance of superconductivity is expected in \(\text{Ta}_2\text{PdSe}_6\) via such co-intercalation.

Here, we have tried to intercalate lithium and ethylenediamine (EDA) \(\text{C}_2\text{H}_8\text{N}_2\) into \(\text{Ta}_2\text{PdSe}_6\) to obtain a new intercalation superconductor.

2. Experimental

Polycrystalline samples of \(\text{Ta}_2\text{PdSe}_6\) were prepared by the solid-state reaction method. Tantalum powder, palladium powder and selenium grains, which were weighed in a molar ratio of \(\text{Ta} : \text{Pd} : \text{Se} = 2 : 1 : 6.18\), were mixed and pressed into pellets. The excess of Se was necessary to compensate for the loss of Se during the reaction due to its high vapor pressure. The pellets were sealed in an evacuated quartz tube and heated at 725°C for 300 h. The obtained pellets were thoroughly pulverized into powder, mixed and then pressed into pellets again and sealed and heated once more. Then, the obtained pellets of \(\text{Ta}_2\text{PdSe}_6\) were pulverized into powder again to be used for the intercalation. The co-intercalation of lithium and EDA into the powdery \(\text{Ta}_2\text{PdSe}_6\) was performed as follows. The powdery \(\text{Ta}_2\text{PdSe}_6\) of 0.7g was placed in a beaker filled with a solution of pure lithium metal dissolved in 7.4 ml of EDA. The amount of Li was set at \(0 \leq x \leq 1.5\) in a molar ratio of \(\text{Li} : \text{Ta}_2\text{PdSe}_6 = x : 1\). The intercalation of only EDA without Li, namely, \(x = 0\) was also tried. The intercalation reaction was carried out at 90°C for 10 days. The product was washed with fresh EDA. All the processes were performed in an argon-filled glove box. Both the host sample of \(\text{Ta}_2\text{PdSe}_6\) and intercalated samples of \(\text{Li}(\text{C}_2\text{H}_8\text{N}_2)\text{Ta}_2\text{PdSe}_6\) were characterized by the powder x-ray diffraction using Cu Ka radiation. For the intercalated samples, an airtight sample-holder was used. The diffraction patterns were analysed using Rietan-FP [15]. The chemical composition was determined by the inductively coupled plasma optical emission spectrometry (ICP-OES). In order to detect the superconducting transition, the magnetic susceptibility \(\chi\) was measured.
using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS). Measurements of the electrical resistivity $\rho$ were also carried out by the standard dc four-probe method. For the $\rho$ measurements, intercalated powdery samples were pressed into pellets at room temperature without heat treatment.

Figure 1. (a) Crystal structure of Ta$_2$PdSe$_6$ with the interlayer spacing between Ta$_2$PdSe$_6$ layers $d = 6.14$ Å. Solid lines represent the unit cell. Schematic views of crystal structures of (b) Phase I of (C$_2$H$_8$N$_2$)$_x$Ta$_2$PdSe$_6$ with $d \sim 10.1$ Å and (c) Phase II of Li$_x$(C$_2$H$_8$N$_2$)$_x$Ta$_2$PdSe$_6$ with $d \sim 11.0$ Å.

3. Results and discussion
A series of Li$_x$(C$_2$H$_8$N$_2$)$_x$Ta$_2$PdSe$_6$ samples with nominal values of $x = 0, 0.5, 1.2, \text{ and } 1.5$ have been confirmed to be synthesized by the powder x-ray diffraction. Figure 2 shows the powder x-ray diffraction patterns of the host sample of Ta$_2$PdSe$_6$ and the intercalated sample of (C$_2$H$_8$N$_2$)$_x$Ta$_2$PdSe$_6$ with $x = 0$. The broad peak around $2\theta = 20^\circ$ is due to the airtight sample holder. The obtained host sample of Ta$_2$PdSe$_6$ is found to be of the single phase, because all the Bragg peaks are able to be indexed on the basis of the monoclinic structure (space group: C2/m). For the intercalated sample of (C$_2$H$_8$N$_2$)$_x$Ta$_2$PdSe$_6$, a sharp Bragg peak is observed at a very small value of $2\theta \sim 9^\circ$, indicating a large expansion of the lattice constant via the intercalation of EDA. It is found that all the Bragg peaks are well indexed on the basis of the monoclinic structure (space group: C2/m), assuming that Ta$_2$PdSe$_6$ layers are much separated by the intercalation of EDA. The lattice constants of the intercalated sample of (C$_2$H$_8$N$_2$)$_x$Ta$_2$PdSe$_6$ are calculated to be $a = 13.466(1) \text{ Å, } b = 3.3705(4) \text{ Å, } c = 14.183(5) \text{ Å, } \beta = 86.15(1)^\circ$.

Figure 2. Powder x-ray diffraction patterns of the host sample of Ta$_2$PdSe$_6$ and the intercalated sample of (C$_2$H$_8$N$_2$)$_x$Ta$_2$PdSe$_6$, using Cu Kα radiation. For reference, the simulated powder x-ray diffraction pattern of the hypothetical compound of Ta$_2$PdSe$_6$ with $a = 13466(1) \text{ Å, } b = 3.3705(4) \text{ Å, } c = 14.183(5) \text{ Å, } \beta = 86.15(1)^\circ$ is also shown. Indices without and with an asterisk are due to the host sample and the intercalated sample, respectively.
Accordingly, it is concluded that EDA has been intercalated between Ta₂PdSe₆ layers. The interlayer spacing between Ta₂PdSe₆ layers d in (C₂H₈N₂)Ta₂PdSe₆ is estimated from the 101 peak to be 10.1 Å and much larger than d = 6.14 Å of the host sample of Ta₂PdSe₆. Since the enhancement of the d value via the intercalation of EDA with the size of 3.7 Å in width and 5.4 Å in length is 4.0 Å, EDA is inferred to be intercalated in parallel between Ta₂PdSe₆ layers, as shown in Fig. 1(b).

Figure 3 shows the powder x-ray diffraction patterns of the host sample of Ta₂PdSe₆ and intercalated samples of Liₓ(C₂H₈N₂)Ta₂PdSe₆ with various nominal values of x. With increasing x, it is found that the 101 peak around 9° (due to Phase I) shifts to around 8° (due to Phase II). This indicates that Phase I with d ~ 10.1 Å of x = 0 changes to Phase II with d ~ 11.0 Å with increasing x. In x = 0.5, Phase I and Phase II are mixed. Phase I is only EDA-intercalated (C₂H₈N₂)Ta₂PdSe₆, as mentioned above. Therefore, Phase II is regarded as both Li- and EDA-intercalated Liₓ(C₂H₈N₂)Ta₂PdSe₆. Since the enhancement of the d value via the intercalation of Li and EDA in Phase II is ~ 4.9 Å and is close to the length of EDA, EDA is inferred to be intercalated perpendicularly to the Ta₂PdSe₆ layers as shown in Fig. 1(c), as in the case of both Li- and EDA-intercalated Liₓ(C₂H₈N₂)Fe₂Se₂ [10].

Figure 4 shows the temperature dependences of χ in a magnetic field of 10 Oe on zero-field cooling (ZFC) and on field cooling (FC) for intercalated samples of Liₓ(C₂H₈N₂)Ta₂PdSe₆ with various nominal values of x. A superconducting transition is observed around 4.5 K in 0 ≤ x ≤ 1.2, while no superconducting transition is observed for x = 1.5. The superconducting volume fraction, simply estimated from the χ value at 2 K on ZFC, is as large as ~ 30 % in x = 0 and markedly decreases with increasing x. On the other hand, Tc is almost constant in 0 ≤ x ≤ 1.2. Accordingly, it is concluded that only Phase I of (C₂H₈N₂)Ta₂PdSe₆ with x = 0 is a bulk superconductor with Tc = 4.5 K, while Phase II of Liₓ(C₂H₈N₂)Ta₂PdSe₆ (x ≠ 0) is not superconducting. That is, the increase of electron carriers by the co-intercalation of Li is harmful to the superconductivity in (C₂H₈N₂)Ta₂PdSe₆.

Figure 3. Powder x-ray diffraction patterns of the host sample of Ta₂PdSe₆ and intercalated samples of Liₓ(C₂H₈N₂)Ta₂PdSe₆ with various nominal values of x, using CuKα radiation. Indices without and with single and double asterisk marks are due to the host sample, Phase I and Phase II, respectively. Peaks marked by ▽ is due to an unknown compound.

Figure 4. Temperature dependences of the magnetic susceptibility χ in a magnetic field of 10 Oe on zero-field cooling (ZFC) and on field cooling (FC) for intercalated samples of Liₓ(C₂H₈N₂)Ta₂PdSe₆ with various nominal values of x.
Figure 5 displays the temperature dependences of $\rho$ for the host sample of Ta$_2$PdSe$_6$ and intercalated samples of Li$_x$(C$_2$H$_8$N$_2$)$_y$Ta$_2$PdSe$_6$ with typical nominal values of $x$. It is found that $\rho$ of Ta$_2$PdSe$_6$ shows a metallic temperature-dependence, while $\rho$ of intercalated samples shows a semiconducting temperature-dependence. A superconducting transition is observed at a low temperature below 4.5K for $x = 0$ and 0.5 including Phase I. The transitions are very broad and zero-resistivity is not observed above 2 K and moreover the absolute values of $\rho$ of intercalated samples are not so small. These are inferred to be due to grain-boundaries in the intercalated pellet samples and may be due to the degradation of the samples caused by the atmospheric exposure in the process of making four terminals on the sample surface for the $\rho$ measurement.

As for the origin of the appearance of superconductivity in (C$_2$H$_8$N$_2$)$_y$Ta$_2$PdSe$_6$, several possibilities are supposed. One is the enhancement of the density of states at the Fermi level owing to the enhancement of the two-dimensionality of the electronic structure caused by the expansion of the interlayer spacing between Ta$_2$PdSe$_6$ layers. Another is the enhancement of the electron-phonon interaction owing to the isolation of each Ta$_2$PdSe$_6$ layer, as pointed out in single-layer FeSe [16]. The other is the contribution of the electronic polarization of EDA to the formation of Cooper pairs. Further investigation is necessary to clarify which the case is. On the other hand, the suppression of superconductivity by the co-intercalation of Li into (C$_2$H$_8$N$_2$)$_y$Ta$_2$PdSe$_6$ may be due to the decrease in the density of states at the Fermi level. The origin of the appearance of superconductivity in (C$_2$H$_8$N$_2$)$_y$Ta$_2$PdSe$_6$ has been supposed as follows. One is the enhancement of the two-dimensionality of the electronic structure.

4. Summary
We have succeeded in synthesizing new intercalation compounds of Li$_x$(C$_2$H$_8$N$_2$)$_y$Ta$_2$PdSe$_6$ with $0 \leq x \leq 1.5$ via the intercalation of only EDA and the co-intercalation of Li and EDA into Ta$_2$PdSe$_6$. In only EDA-intercalated (C$_2$H$_8$N$_2$)$_y$Ta$_2$PdSe$_6$, $d = 10.1$ Å and EDA has been inferred to be intercalated in parallel between Ta$_2$PdSe$_6$ layers. In both Li- and EDA-intercalated Li$_x$(C$_2$H$_8$N$_2$)$_y$Ta$_2$PdSe$_6$, with increasing $x$, it has been found that Phase I with $d \sim 10.1$ Å changes to Phase II with $d \sim 11.0$ Å, where EDA is inferred to be intercalated perpendicularly to Ta$_2$PdSe$_6$ layers. From $\chi$ and $\rho$ measurements, it has been concluded that only EDA-intercalated (C$_2$H$_8$N$_2$)$_y$Ta$_2$PdSe$_6$, namely, Phase I is a bulk superconductor with $T_c = 4.5$ K and that both Li- and EDA-intercalated Li$_x$(C$_2$H$_8$N$_2$)$_y$Ta$_2$PdSe$_6$, namely, Phase II is not superconducting. Therefore, the electron doping by the co-intercalation of Li is harmful to the superconductivity in (C$_2$H$_8$N$_2$)$_y$Ta$_2$PdSe$_6$, which may be due to the decrease in the density of states at the Fermi level. The origin of the appearance of superconductivity in (C$_2$H$_8$N$_2$)$_y$Ta$_2$PdSe$_6$ has been supposed as follows. One is the enhancement of the two-dimensionality of the electronic structure.
Another is the enhancement of the electron-phonon interaction. The other is the contribution of the electronic polarization of EDA to the formation of Cooper pairs.

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