First-principles study of hydrogen-bonded molecular conductor
κ-H₃(Cat-EDT-TTF/ST)₂

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We theoretically study hydrogen-bonded molecular conductors synthesized recently, κ-H₃(Cat-EDT-TTF)₂ and its diselena analog, κ-H₃(Cat-EDT-ST)₂, by first-principles density-functional theory calculations. The band structure near the Fermi level shows a quasi-two-dimensional character, with a rather large interlayer dispersion due to the absence of insulating layers as in charge transfer salts. In these crystals, two H(Cat-EDT-TTF/ST) units share a hydrogen atom with a short O–H–O hydrogen bond. We show that an effective half-filled model on an anisotropic triangular lattice can be constructed based on dimers of H(Cat-EDT-ST/ST) units which are face-to-face to each other but, not connected by the hydrogen bond. Furthermore, we find a a stable structure where the shared H atom becomes localized to one of the O atoms; there, charge disproportionation between the two types of H(Cat-EDT-TTF) units is associated. Nevertheless, the calculated adiabatic potential energy surface for the H atom is very shallow near the minimum points, therefore the probability of the H atom can be delocalized between the two O atoms.

I. INTRODUCTION

A new class of molecular conductors containing hydrogen bonds (H-bonds) has been developed recently. The compounds are based on catechol with ethylenedithiotetraethielfulvalene molecules, Cat-EDT-TTF and its diselena analog ethylenedithio-selenathiafulvalene, Cat-EDT-ST. Among them, κ-H₃(Cat-EDT-TTF)₂ (space group: C2/c, abbreviated here as κ-S) is considered to be a Mott insulator where each dimer of H(Cat-EDT-TTF) units possesses a localized spin $S = 1/2$ at ambient pressure, and its physical properties indicate the possible realization of a quantum spin-liquid (QSL) state; despite the exchange interaction of about 80 – 100 K, the magnetic susceptibility shows no magnetic ordering down to 2 K, and the magnetic torque shows a paramagnetic behavior even at 50 mK. On the other hand, its isostructural diselena analogue, κ-H₃(Cat-EDT-ST)₂ (abbreviated here as κ-Se), also an insulator, turns to show a metallic behavior at room temperature by the application of pressure above 1.3 GPa, where the room-temperature electric conductivity increases up to 180 S/cm at 2.2 GPa; κ-S remains insulating up to about 1.6 GPa. This conductivity observed in κ-Se is the highest among molecular conductors. It is also reported that a deuterium (D) substitution for κ-S induces a non–magnetic charge disproportionated state associated with D localization.

A notable difference from conventional charge transfer-type molecular conductors is that these compounds do not have discrete insulating layers. The molecular structure of the H₃(Cat-EDT-TTF/ST)₂ unit is illustrated in Fig. 1(a) whose geometry is taken from the crystal structure of κ-S shown in Fig. 1(b). Two H(Cat-EDT-TTF/ST) units share a H atom with a relatively short O–H–O hydrogen bond (e.g. O···O length in κ-S: 2.45 Å). The shared H atom is centered at the middle of two nearest O atoms with O–H lengths of 1.23 Å. These geometries...
tries are in accordance with the systematic survey of the correlation between O–H and O···O lengths in H-bonds for a large number of material systems. An important issue is whether essential differences exist in their electronic structure compared with charge transfer salts, especially considering the role of H-bonds and their consequence on the electronic properties of these systems.

Proton dynamics in such short intermolecular H-bonds play essential roles in various functional molecular materials such as organic ferroelectrics, molecular conductors, and biochemical reactions. In general, the shape of the potential for H in such short H-bonds is sensitive to the O···O distance. For such systems, the H position and its influence to the relevant electronic structure are crucially important. However, it is difficult to determine the H position using neutron scattering techniques due to their small size of samples. Therefore, first-principles calculation is a useful tool to clarify such properties.

In this work, we investigate the electronic and structural properties of κ-S and κ-Se by first-principles density-functional theory (DFT) calculations. We report unique properties of the electronic structure compared with conventional charge transfer salts, as well as the differences between these two compounds. We evaluate transfer integrals by fitting the DFT band structures and discuss its possible relevance to the QSL state observed in κ-S. Concerning the H-bonds, we calculate the adiabatic potential surface to investigate the degree of localization of the shared H atom, and discuss the sensitivity of the electronic structure depending on the H position.

II. COMPUTATIONAL DETAILS

The first-principles DFT calculations were performed by all-electron full-potential linearized augmented plane wave (FLAPW) method as implemented in the QMD-FLAPW12 code. We used the exchange-correlation functional of the generalized gradient approximation (GGA) by Perdew-Burke-Ernzerhof. Non-spin-polarized calculations were performed. In the first part, we use experimental lattice parameters and atomic positions of base-centered monoclinic structure with the space group C2/c; these structures of κ-S and κ-Se were measured at 50 K and 30 K, respectively. We optimized only for all H positions to set up suitable sizes of muffin-tin spheres since the experimental geometries show shorter O–H distances with the chemical bonds. In the latter part of this paper, we also show results in which all the atomic positions are optimized. There, we consider cases lowering the space group C2/c, but preserving the unit cell, which allows the shared H position to displace from the symmetric point.

III. RESULTS AND DISCUSSIONS

A. Experimental structure

Figures (a) and (b) show the calculated band structures of κ-S and κ-Se, respectively, where both show quasi-two-dimensional (2D) electronic structures. There are four bands near the Fermi level. The unit cell contains twice of the chemical formula H₃(Cat-EDT-TTF/ST), i.e., two dimers of H(Cat-EDT-TTF) units, and each H(Cat-EDT-TTF/ST) unit provides one degree of freedom [see Fig. 3 for their 2D packing structure]. The upper two bands cross the Fermi energy; they are half-filled and composed of antibonding states of two H₃(Cat-EDT-TTF/ST) units. These features are analogous to the known dimer-Mott insulators such as κ-(BEDT-TTF)₂X whose the half-filled valence band consists of the antibonding combination of the HOMO of the BEDT-TTF molecules. Comparing the band structures between the two, κ-Se has a larger bandwidth of 359 meV than that of κ-S, 312 meV. This comes from delocalized...
character of Se–p orbitals than S–p orbitals. A notable point is that the bands along the Y–Γ direction are rather dispersive, i.e., the existence of a relatively large three-dimensionality of the electronic structure. This originates from the absence of insulating layers between electron conducting layers, which is peculiar to κ-S and κ-Se; this is seen in the estimated transfer integrals as in the following.

In Table I, we list the transfer integrals obtained by four- and two-bands fitting based on monomers of H(Cat-EDT-TTF/ST) unit, and its dimers, respectively. Their definitions are illustrated in Fig. 3(a) and (b), respectively. For κ-S, the transfer integrals obtained by the four-bands fitting to the DFT bands agree well with those obtained by the extended Hückel method. On the other hand, for κ-Se, there are quantitative differences between them. In both compounds, a transfer integral 1 where a face-to-face overlaps of the molecules within the dimers is seen, is the largest. The second largest 2, where the overlap of C– and S–p orbitals in one unit with those in the nearest dimer exists, determines the bandwidth. The three-dimensionality mentioned above is seen in the inter-layer transfer integrals; they are not negligible compared with intra-layer values. Comparable values of ~10 – 20 meV are found along two interlayer bonds l1 and l2 (see Fig. 4) in both compounds. These two are comparable to an intra-layer q, and were needed for a reasonable fitting to the dispersive bands along the Y–Γ direction. In κ-Se, the transfer integral along 2 is larger than that in κ-S; this is the main reason for the larger bandwidth of κ-Se than κ-S.

Among the transfer integrals obtained by the two-bands fitting, the largest two, those along 2 and p, form an anisotropic triangular lattice, similarly to the case of κ-(BEDT-TTF)2X. We find that the value along one side (2) of an isosceles triangle is stronger than that along the two equal sides (p). The ratio of our inter-dimer transfer integrals, 2/p which is known as t'/t in the literature applied to different compounds is estimated as 1.25 and 1.42 for κ-S and κ-Se, respectively. The extended Hückel calculations give the ratio of 1.48 and 1.66, respectively. Then, one view of the electronic structure is that one-dimensional chains formed by the 2 bonds are connected by frustrated inter-chain couplings along the p bonds. Similar tendency was reported in first-principles studies for β’-EtMe3Sb[Pd(dmit)2]2 which also shows a QSL. Several model calculations also suggest the importance of such an anisotropy for the appearance of QSL. An important point which is peculiar to κ-S and κ-Se is the existence of the relatively large inter-layer transfer integrals, also obtained by the two-bands fitting also show two comparable values of ~10 meV, along L1 and L2 bonds (see Fig. 4), which is expected to act as an inter-layer spin-frustration effect.

### Table I: Inter-molecular (four-bands model) and inter-dimer (two-bands model) parameters obtained by fitting to first-principles band structure. The unit of transfer integrals are meV.

| Intermolecule | b1 | b2 | p  | q  | l1 | l2 |
|---------------|----|----|----|----|----|----|
| κ-S DFT       | 241| 75 | 40 | 11 | 14 | 17 |
| Hückel        | 230| 85 | 46 | 12 |    |    |
| κ-Se DFT      | 258| 98 | 42 | 18 | 14 | 19 |
| Hückel        | 318| 140| 63 | 21 |    |    |

| Interdimer    | Method | b2 | p  | r  | b2/p | L1  | L2  |
|---------------|--------|----|----|----|------|-----|-----|
| κ-S DFT       |        | 32 | -26| -4 | 1.25 | -9  | 10  |
| κ-Se DFT      |        | 44 | -31| -5 | 1.42 | -9  | 11  |

![FIG. 3: (Color online) View of the crystal structure along the a-axis showing bc-plane. Definition of (a) inter-dimer and (b) inter-molecular transfer integrals are presented.](image317x428 to 562x739)

### B. Theoretically optimized structure

Next let us turn to the role of the H-bonds, which is characteristic in these molecular conductors. We first investigate the possibility that the H atom binds to one of the two O atoms in spite of the experimental results. As explained before, the band structures shown in Fig. 2(a) are calculated using the experimental atomic positions with the space group C2/c. With the constraint of this
symmetry adopted from experiments, the shared H atom
situates at the middle point between O1 and O2 atoms;
these two O atoms as well as the attached two H(Cat-
EDT-ST) units are crystallographically equivalent
to each other. Even after we displace the H atom slightly
from the center position and perform the relaxations for
all the atomic positions, the optimized structure is found
to be the same as the one obtained with \( C_2/c \). This
means that the \( C_2/c \) structure is at least one of the local–
minimum structures, even within the classical treatment
of H atom. Then, we moved the H atom more (the O1–H
distance was set to be 1.0 \( \text{\AA} \)), placing it to a position
more closely to O1, and then relaxed the positions of
the all the atoms. As a result, we found another local–
minimum structure where H is localized near O1. It does
not preserve \( C_2/c \); the space group is lowered to \( P\bar{1} \) by
removing the glide symmetry. This structure is energetically
close to the optimized \( C_2/c \) structure; the \( P\bar{1} \) structure is slightly favorable than \( C_2/c \), but the energy
difference is small (1.3 meV/f.u. \( \sim 15 \text{ K} \)).

The crystal structure of the H-localized \( P\bar{1} \) state and
its parameters around the H-bonds are shown in Fig. 5
and Table. II respectively. The O–O length in the
\( P\bar{1} \) structure is 2.44 \( \text{\AA} \), which is slightly longer than in
\( C_2/c \), and now there are two inequivalent O–H distances
which are remarkably different, 1.31 and 1.13 \( \text{\AA} \), re-
spectively. This indicates that there are two types of con-
sisting molecules, \( H_2(\text{Cat-EDT-TTF}) \) and \( H(\text{Cat-EDT-
TTF}) \), abbreviated as w-H and w/o-H units in the follow-
ing, showing small but noticeable structural differences,
especially around the H-bonds (Table. II).

Let us compare the electronic properties for the two
different structures. The band structure of the optimized
\( C_2/c \) and \( P\bar{1} \) structures is shown in Fig. 6(a) and (b).
[The band structure in Fig. 6(a) is almost the same as
that in Fig. 2(a) for the experimental structure with op-
timized H positions; the symmetric lines in Fig. 6 are
those for the \( P\bar{1} \) structure for comparison.] Although the
atomic positions are different between these two struc-
tures, the band structures are found to be very similar
and the width of the two bands crossing the Fermi level is
almost the same. However, we can see the splitting of the
bands near the Fermi level along the M (E)–U–Z line. By
analyzing Kohn-sham wavefunctions (i.e. M (E), U and
Z-points), the splitting bands with index 205 and 208 in
Fig 6(b) are mainly composed of bonding and antibond-
ing states of w/o-H units and that with 206 and 207 are
those of dimers of the w-H units.

![FIG. 5: (Color online) Structural properties around hydro-
gen bonds in H-localized structure (\( P\bar{1} \)) of \( \kappa-H_3(\text{Cat-EDT-
TTF})_2 \). Dotted line shows the unit cell. The shared H atom
is located at the fractional coordinate of (0.01, –0.01, 0.242 [It
is at (0.01, –0.01, 1/4) in the \( C_2/c \) structure.])](image)

### Table II: Theoretically optimized and experimentally de-
termined structural parameters around hydrogen bonds in \( \kappa-
H_3(\text{Cat-EDT-TTF})_2 \). The atom indexes are defined in Fig. 5.

| Space group   | DFT calculations | Expt. (50 K)* |
|---------------|-----------------|--------------|
| H-bond type   | \( C_2/c \)     | \( P\bar{1} \) |
| \( d(O1\cdots O2) [\text{\AA}] \) | 2.43            | 2.44          |
| \( d(O1-H/O2-H) [\text{\AA}] \) | 1.22            | 1.13/1.31     |
| \( \angle O1-H-O2(1) [\text{deg.}] \) | 173.2°         | 173.0°/168.3° |
| \( d(O1-C1) [\text{\AA}] \) | 1.34            | 1.35          |
| \( d(O2-C2) [\text{\AA}] \) | 1.34            | 1.32          |
| \( d(O1\cdots O3) [\text{\AA}] \) | 2.78            | 2.76          |
| \( d(O2\cdots O4) [\text{\AA}] \) | 2.78            | 2.79          |

*Experimental atomic positions were determined by X-ray
diffraction method without any DFT optimizations.
The comparison of the local density of states (LDOS) also clearly indicates a difference of the electronic structure. (Fig. 6(c)) In the occupied state of the energy region around $-0.07$ eV, compared to the case of the $C2/c$ structure where all the H(Cat-EDT-TTF) units are equivalent, the LDOS from the w-H unit increases but that of the w/o-H unit decreases. On the other hand, above the Fermi level from 0 to $+0.2$ eV, the LDOS shows the opposite behavior. This result suggests that a small amount of charge transfer from the w/o-H to the w-H unit. It should be noted that GGA often underestimates the degree of charge disproportionation. If we employ hybrid-functional methods like Heyd-Scuseria-Ernzerhof\textsuperscript{34} or B3LYP\textsuperscript{35} functional, the band structures may show a finite energy gap even in the non-magnetic calculations (band insulator). However, here, we would like to emphasize that even in GGA, a stable structure which breaks the $C2/c$ symmetry is found theoretically and shows a different electronic structure owing to the charge disproportionation between two types of molecules.

\section{Quantum effects}

Lastly, we discuss the quantum effects of the shared H atom. As shown above, we found a structure where the H atom locates close to O1, but there is a possibility that the quantum motion or tunneling of the proton makes it delocalized.\textsuperscript{5} To estimate the degree of localization of the proton wavefunction, we plot the adiabatic potential energy curve using the DFT total energies by changing the $z$-coordinate of the H position, where the positions of all the other atoms are fixed at the optimized $P1$ structure. As shown in Fig. 7, the potential curve has a well-defined minimum-point. We also plot the potential surface for the localized state which the H atom close to the O2 atom (open squares on broken curve). When the distance between the two minima is sufficiently short and adiabatic potential between the minima is shallow near the minimum points, the proton wavefunction becomes centered at the bond midpoint.\textsuperscript{17,20} This is actually the case here, and then we expect that the distribution of the proton can not be localized near the minimum point close to O1 or O2. The distribution should be the highest at the center of O1 and O2, and the H atom appears to be shared by the two O atoms. An interesting point is that the QSL state in $\kappa$-S compound is realized in the $C2/c$ structure where the dimers of H(Cat-EDT-TTF) unit are all crystallographically equivalent and can carry $S = 1/2$ each. This is probably what is happening in the actual material; the $C2/c$ structure is realized by such H delocalization in terms of the quantum motions of the
protons. In clear contrast, in the $P\overline{1}$ structure showing the charge disproporionate states, the existence of two kinds of dimers should break this situation. The quantum effects have an important role for the realization of localized spins in $\kappa$-S.

We also note that, in general, H-localized states with asymmetric O–H–O bonds have relatively larger curvature of the potential at the minimum-point, and their zero-point motion in terms of kinetic energy becomes higher (lower in energy) than those of the symmetric bonds. However, in this system, the curvature at the minimum-point of the H-localized ($P\overline{1}$) structure is small and not remarkably different from that of the $C2/c$ structure having a single minimum (solid circles in Fig. 7). Therefore, the difference of zero-point energy should be small, resulting in a subtle situation where these two structures are energetically very competitive each other.

Then, by substituting D atom for the shared H atom, it is natural to expect that D to be localized around one of two O atoms due to the reduction of quantum fluctuation. In fact, deuterated samples of $\kappa$-S were recently synthesized, and their X-ray diffraction shows that D atom is localized at a position closer to one of the O atoms at low temperature and the O···O length is expanded (2.50 Å). Such expansion in nearly linear O–H–O bond has been known as Ubbelohde effect. Even in D case, we expect that the relative stability between the $P\overline{1}$ and $C2/c$ structures is very subtle as well. Further studies such as theoretical relaxations with hybrid-functionalons are desired in the near future.

IV. CONCLUSION

We have investigated structural and electronic properties of $\kappa$-H$_3$(Cat-EDT-TTF)$_2$ and $\kappa$-H$_3$(Cat-EDT-ST)$_2$ by first-principles DFT calculations. We evaluated transfer integrals by fitting to the DFT bands, and found a quasi-one-dimensional anisotropy in the effective inter-dimer interactions with frustrated inter-chain couplings; the ratio of our inter-dimer transfer integrals, $b_2/p$ which is known as $t'/t$, is 1.25 and 1.42 for $\kappa$-S and $\kappa$-Se, respectively. $\kappa$-Se has a larger band width and stronger 1D anisotropy compared to $\kappa$-S. Two relatively large inter-layer transfer integrals were found, corresponding to the three-dimensionality of the electronic structure due to the absence of insulating layers. As for H-bonds, we found a H-localized phase by structural optimization. It shows charge imbalance in the LDOS associated with two different H(Cat-EDT-TTF) dimers. Since the bottoms of the calculated adiabatic potential wells are very shallow, the probability of the H atom can be delocalized between two O atoms when the quantum fluctuation of the H atom position is considered, and makes it competitive to the $C2/c$ structure.

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LAPW basis with a cut-off of $|k + G| \leq 5.5$ a.u. were used. Muffin-tin (MT) sphere radii are set to be 1.96 a.u. for S, 1.15 a.u. for O, 1.28 a.u. for C, and 0.68 a.u. for H atoms. For Brillouin zone integrations, $5 \times 5 \times 3$ k-points mesh are used.

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