Supplementary information

for

Antiferromagnetic ordering and signatures of enhanced spin-frustration in honeycomb-layered tellurates with Ag bilayers

Sachio Komori1*, Kohei Tada2*, Noboru Taguchi2, Tomoyasu Taniyama1, Titus Masese2*

1Department of Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan
2Research Institute of Electrochemical Energy, National Institute of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan
* komori.sachio.h0@f.mail.nagoya-u.ac.jp   *k-tada@aist.go.jp   *titus.masese@aist.go.jp

1. Interslab exchange coupling in honeycomb-layered tellurates

To investigate an interslab magnetic exchange coupling of (Te, M)-O magnetic layers through a cationic layer (denoted X layer), we have calculated the total energy difference between layered-antiferromagnetic (L-AFM) and ferromagnetic (FM) ordering \[ \Delta E = E(\text{FM}) - E(\text{L-AFM}) \] for various X layers, which are plotted in Fig. S1 (left-axis). Larger \( \Delta E \) indicates larger interslab exchange coupling (the L-AFM state is more stable than the corresponding FM state due to the exchange coupling). \( \Delta E \) exponentially decreases with increasing thickness of the X layer (right-axis of Fig. S1). Although the ionic radius of Ag\(^+\) is comparable to Na\(^+\), a dumbbell-like straight coordination through the d-orbital of Ag\(^+\) results in a large interslab distance and a stronger suppression of the interslab magnetic exchange coupling in Ag\(_{2-x}\)M\(_2\)TeO\(_6\) (0 < x < 2) than that in Na\(_2\)M\(_2\)TeO\(_6\). Moreover, the interslab distance of Ag\(_2\)M\(_2\)TeO\(_6\) is even longer (9 Å\(^2\)) than that of Ag\(_{2-x}\)M\(_2\)TeO\(_6\) (6 Å\(^2\)), implying a further suppression of the magnetic exchange coupling due to the presence of Ag bilayers.

The exchange-correlation functional used for the density functional theory (DFT) calculation was the generalised gradient approximation formula of Perdew-Burke-Ernzerhof (GGA-PBE) [1], and the basis set was plane-wave with projector-augmented-wavefunction (PAW) method [2]. The electrons in the inner core regions were treated by PAW, and the numbers of valence electrons of Li, Na, K, Rb, Ag, Ni, Te, and O were 1 (2s\(^1\)), 1 (3s\(^1\)), 7 (3p\(^6\)4s\(^1\)), 7 (4p\(^6\)5s\(^1\)), 11 (4d\(^{10}\)5s\(^1\)), 10 (3d\(^{10}\)4s\(^2\)), 6 (5s\(^2\)5p\(^4\)) and 6 (2s\(^2\)2p\(^4\)), respectively. The energy cut-offs for wavefunction and augmented charge were 500 eV and 2400 eV. To correct repulsions among the 3d electrons of Ni, DFT+U method was used (the applied \( U \) value was 4.0 eV) [3]. Dispersion forces were corrected by DFT-D3 scheme using the parameter with
Becke-Jonson damping [4]. The sampled \( k \)-points were on the \( \Gamma \)-centred mesh of \( 5 \times 5 \times 3 \). The DFT calculations were performed by VASP programme [5].

Due to the non-subtleties of pseudo-spin simulation using Kohn-Sham formalism in VASP, we considered the simulation of the recently predicted Ag degenerate states in Ag bilayers\(^6\) as beyond our present scope. Even if a pseudo-spin moment of Ag bilayered structures presents, the small moment is unlikely to affect the interslab exchange coupling and therefore the Ag-bilayered \( \text{Ag}_6\text{Mg}_2\text{TeO}_6 \) should also follow the trend in Fig. S1.

**Fig. S1** (a) Difference of the total energy between FM and layered (L)-AFM states (left-axis) and interslab distance (right-axis) for mono-layered \( \text{X}_2\text{M}_2\text{TeO}_6 \) with a single cationic X layer (\( \text{X} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{and Ag} \)). (b) Schematic views of L-AFM and FM spin configurations. (c) Schematic view of \( \text{(Te, M)} \)-O magnetic layers separated by a distance \( L \). Crystal structures of \( \text{X}_2\text{M}_2\text{TeO}_6 \) with \( \text{X} = \) (d) Li, (e) Na, (f) K, (g) Rb, and (h) Ag.
2. Magnetic properties of Ag$_2$Mg$_2$TeO$_6$

To investigate the presence of pseudo-spins in the Ag-bilayers, we measured magnetic properties of Ag$_2$Mg$_2$TeO$_6$ ($M = \text{Mg}$) which does not have magnetic honeycomb slabs and therefore suitable to detect the moment from the pseudo-spins. Figure S2(a) shows the magnetic susceptibility ($\chi$) versus temperature ($T$) curve at the magnetic field ($H$) of 100 Oe. $\chi$ at 300 K is about 3 orders of magnitude smaller than that of $M = \text{Co}, \text{Co}_{0.5}\text{Ni}_{0.5}$, and Ni [Figs. 2(a)-(c) in the main paper]. Although an increase of $\chi$ with decreasing $T$ is observed, the $T$-dependence deviates from the Curie-Weiss law, suggesting that a paramagnetic moment is not predominant in $M = \text{Mg}$, which is in sharp contrast to $M = \text{Co}, \text{CoNi}$, and Ni. From moment versus field [$m(H)$] curve at 10 K [Fig. S2(b)], we identify a small fraction of ferromagnetic ordering with the saturation moment and field of about 0.1 emu mol$^{-1}$ and 1 kOe, respectively. The ferromagnetic ordering is also observable in $M = \text{Co}, \text{Co}_{0.5}\text{Ni}_{0.5}$, and Ni, which manifests as a peak near zero field in their $dm/dH$ curve as shown in Fig. S2(c). However, further study is necessary to clarify the relation between the ferromagnetic order and the pseudo-spins in the Ag bilayers.

Fig. S2 (a) $\chi$ versus $T$ at $H = 100$ Oe measured during cooling and (b) $m$ versus $H$ at $T = 10$ K for Ag$_2$Mg$_2$TeO$_6$ ($M = \text{Mg}$) polycrystalline powders. (c) $dm/dH$ versus $H$ for at $T = 10$ K for $M = \text{Co}$ (the red curve), Co$_{0.5}$Ni$_{0.5}$ (the green curve), and Ni (the blue curve).

3. Estimation of the spin-flop transition field

In Fig. S3(a), we plot the temperature dependence of the $m(H)$ curve for $M = \text{Co}_{0.5}\text{Ni}_{0.5}$. At low temperatures (4 K and 20 K) below the Néel temperature ($T_N$), the $m(H)$ curve is non-linear, indicating the presence of a broad spin-flop transition. Figure S3(b) shows the $m(H)$ and $dm/dH (H)$ curves at 10 K for $M = \text{Co}_{0.5}\text{Ni}_{0.5}$. We have estimated the transition field from the field giving the maximum of $dm/dH$
We note that the transition can occur in a broad field range around $H = 60 \text{ kOe}$ due to factors such as a size variation of the polycrystalline powder sample.

**Fig. S3** (a) $m$ versus $H$ at $T = 4$ (the blue curve), 20 (the black curve), 30 K (the red curve) for $M = \text{Co}_{0.5}\text{Ni}_{0.5}$. (b) $m$ (the red curve; left-axis) and $dm/dH$ (the blue dots; right-axis) versus $H$ at $T = 10$ K for $M = \text{Co}_{0.5}\text{Ni}_{0.5}$.


