Supplemental Material for "Flat-Band Ferromagnetism in $Pb_2Sb_2O_7$ by Self-Doped Mechanism"

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In this Supplemental Materials we present the detail of the band structure calculation and the tight-binding analysis of $Pb_2Sb_2O_7$.

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I. DETAILS OF THE DFT CALCULATIONS

Based on the density-functional theory (DFT), we have calculated the electronic structure of $Pb_2Sb_2O_7$ from first-principles for pyrochlore and webelite structures. We have used a full-potential augmented plane-wave (FLAPW) scheme and the exchange-correlation potential was constructed within the general gradient approximation (GGA)[1]. As for the computing code we used the WIEN2k package[2]. The parameter RK_{max} is chosen as 7.0. The k-point mesh is taken so that the total number of mesh in the first Brillouin zone is ~ 1000. The convergence of atomic position is judged by the force working on each atom is less than 1.0 mRy/a.u. We optimized lattice constant and atomic coordinates while keeping the space group to $Fd\bar{3}m$ (No.227) for the pyrochlore structure. Under this restriction, the only one structural parameter to be optimized is u of O(u,1/8,1/8). We have obtained the lattice parameter $a = 10.8804$ Å,which is close the experimental data[3]. We could not find experimental value of u in the literatures, but our optimized u value was $u = 0.43241$, which is close to the value of u in other pyrochlore oxide $Sn_2Nb_2O_7$. After the optimization of the crystal structure, we also included the spin-orbit interaction (SOI) by the second-variational manner. As explained in the main text, the valence band which includes the quasi-flat band mainly consists of Pb-s and O′-p orbitals. Therefore the effect of SOI is very small with respect to the valence band width (Although Pb is a heavy atom, Pb-s orbital does not have angular momentum). For example, the energy splitting due to SOI indicated in Fig. 1(d) is only ~ 35 meV at Γ point.

As for weberite structure, we only used experimental lattice parameters and atomic positions due to the complexity of the crystal structure[4]. Nevertheless, we found that the weberite structure is more energetically favored than the pyrochlore structure. The obtained value 0.644 eV per $Pb_2Sb_2O_7$ gives a lower bound for the stabilization energy of the weberite phase.

We show the DOS and the energy dispersion of $Pb_2Sb_2O_7$ for the weberite structure in Fig. S1. For the weberite structure we obtained a band gap of 2.08 eV, and there is no feature of the flat band.

II. DETAILS OF THE TIGHT-BINDING CALCULATIONS

We used the calculation code Wannier90[5], which constructs maximum localized Wannier functions (MLWFs) directly from the *ab-initio* energy bands. As for MLWFs, we used localized orbitals which have the same symmetry with the corresponding atomic orbitals like Pb-s and Sb-s.

The MLWFs are constructed from the *ab initio* eigenvalues and eigenvectors on the $8 \times 8 \times 8$ unshifted k-mesh points. The obtained tight-binding model is 4-orbital model with including many transfer (or hopping) integrals other than the nearest neighbor atoms. We can perfectly reproduce the original bands using 'Pb-s' MLWFs as shown in Fig. 1(b) in the main text (green curves, FB1), though the bottom of these bands (at Γ point with energy ~ -2.7 eV) is entangled with O-p bands. Similarly, the bottom of the conduction band can perfectly described by 'Sb-s' MLWFs as shown in Fig.1(c) in the main text (green curves, FB2), though the top of these bands (at Γ point with energy ~ 3.0 eV) is entangled with higher energy bands. We show the four largest parameters of these tight-binding models

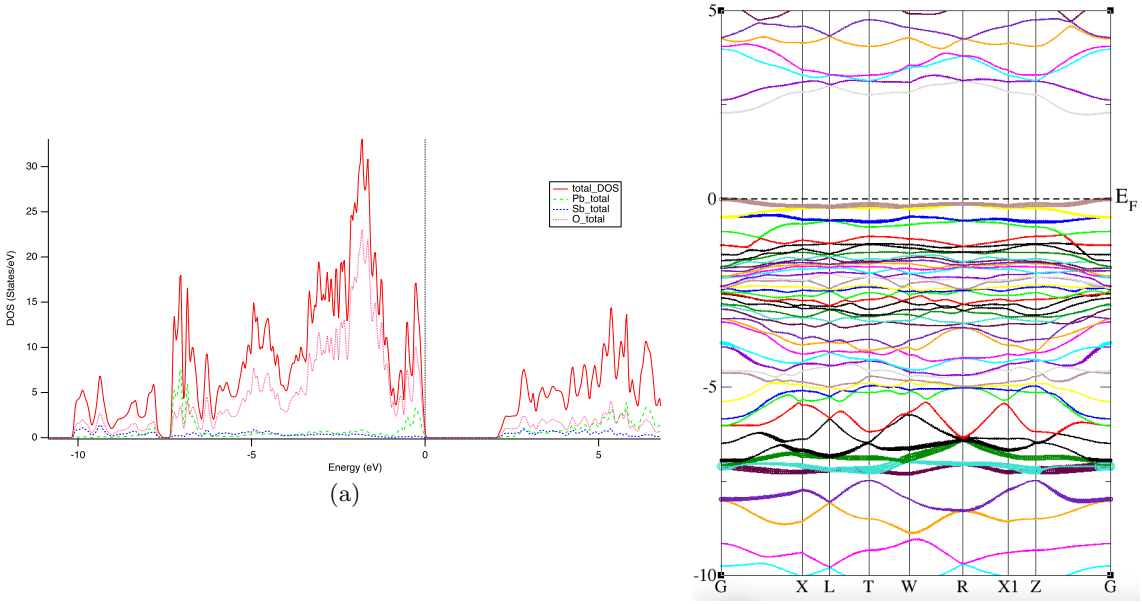

FIG. 1: (a) DOS curve and (b) energy dispersion of $Pb_2Sb_2O_7$ for the weberite structure.

in Table I(a) and I(b). See the main text for further discussion.

[1] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[2] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvashnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Vienna University of Technology, Vienna 2001).
[3] F. Brisse, D. J. Stewart, V. Seidl and O. Knop, Can. J. Chem. **50**, 3648 (1972).
[4] S. A. Ivanov and V. E. Zavodnik, Sov. Phys. Crystallogr. **35**, 494 (1990).
[5] A. A. Mostofi, J. R. Yates, Y. -S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comput. Phys. Commun. **178**, 685 (2008).