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# Charge localization, frustration relief, and spin-orbit coupling in $\text{U}_3\text{O}_8$

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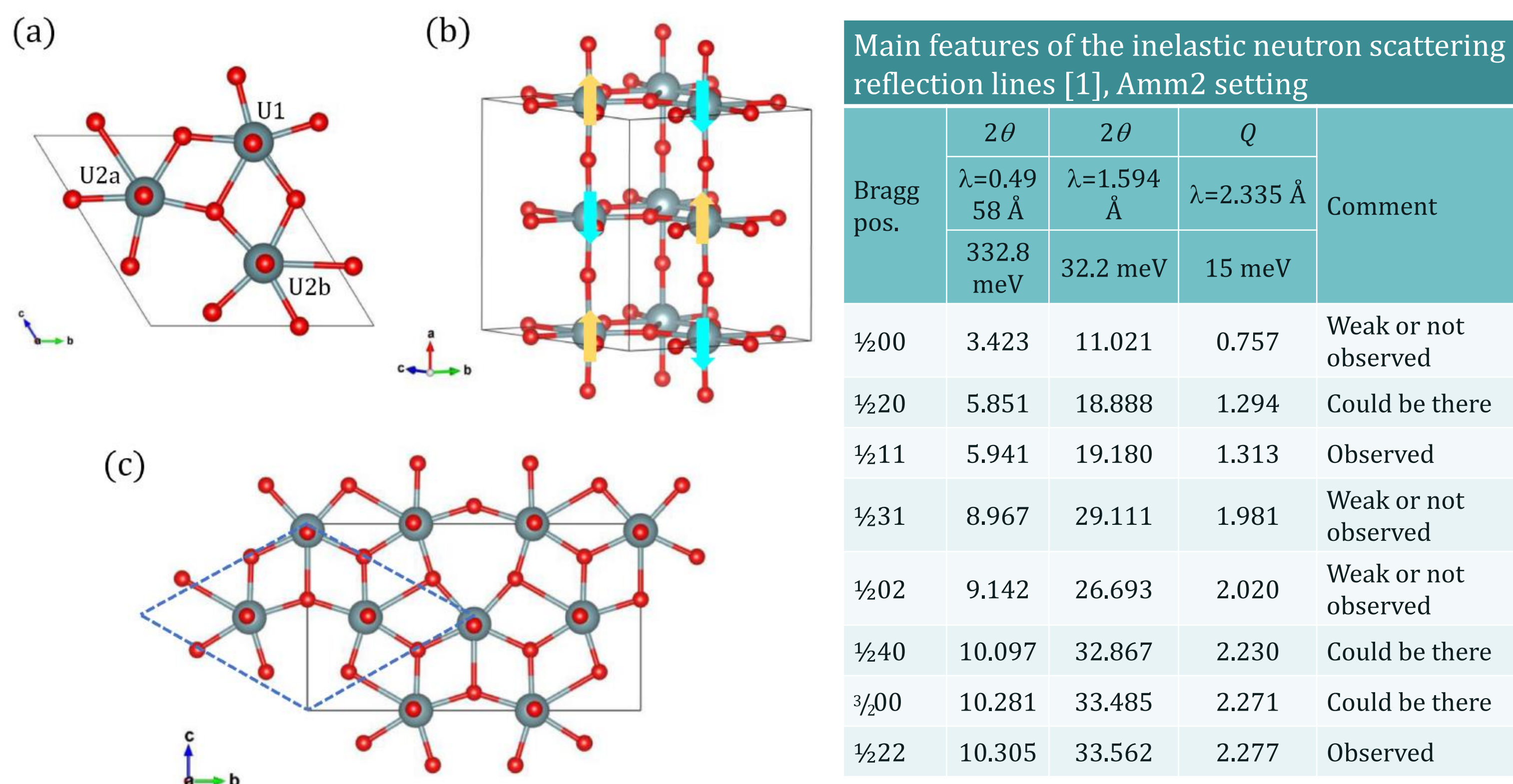
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## Abstract

In spite of continued research efforts over the past several years, the understanding of the magnetic order and electronic properties of  $\text{U}_3\text{O}_8$  has proved elusive so far. Based on published neutron magnetic scattering data and DFT-based methods we show that 1) anisotropic effective spin interactions induce a collinear magnetic order in this layered system, with antiferromagnetic (AFM) coupling both in-layer and between layers, 2) charge localization transforms the in-layer triangular lattice of U atoms into a slightly distorted honeycomb lattice with Néel-type AFM ground-state, while relieving the initial AFM order topological frustration; the in-plane long range order is stabilized at finite temperature thanks to the interlayer coupling, and 3) spin-orbit coupling has a giant effect on the conduction band. Recent optical absorption measurements strongly support our results.

## Crystal structure

The paramagnetic structure in the low temperature (ground state) phase is orthorhombic, with space group  $Amm2$  (#38) (equivalently,  $C2mm$ ). The phase with magnetic order has a primitive cell with monoclinic symmetry, space group  $Pm$  (#6), as shown below.



There are two types of U atoms in the primitive cell. Reflections of the type  $(\frac{1}{2} L L)$  imply a doubling of the unit cell in the  $a$  direction. Because of symmetry, U1 (Fig. (a) above) cannot bear a magnetic moment, while U2a and U2b have opposite magnetization, as shown in Fig. (b). Figure (c) shows the relation of the monoclinic cell to the  $Amm2$  orthorhombic cell.

## Electronic structure

The electronic structure was calculated with the VASP code, using the projector augmented-wave (PAW) method and the PBE+ $U$  approximation to the exchange-correlation functional, as implemented in that code [2]. The effective  $U_{\text{eff}}$  was taken to be  $U-J=3.96$  eV [3]. The energy cut-off was set to 600 eV; energies were converged to within  $10^{-6}$  eV and forces to 0.03 eV/Å. Spin-orbit coupling (SOC) was included in all calculations.

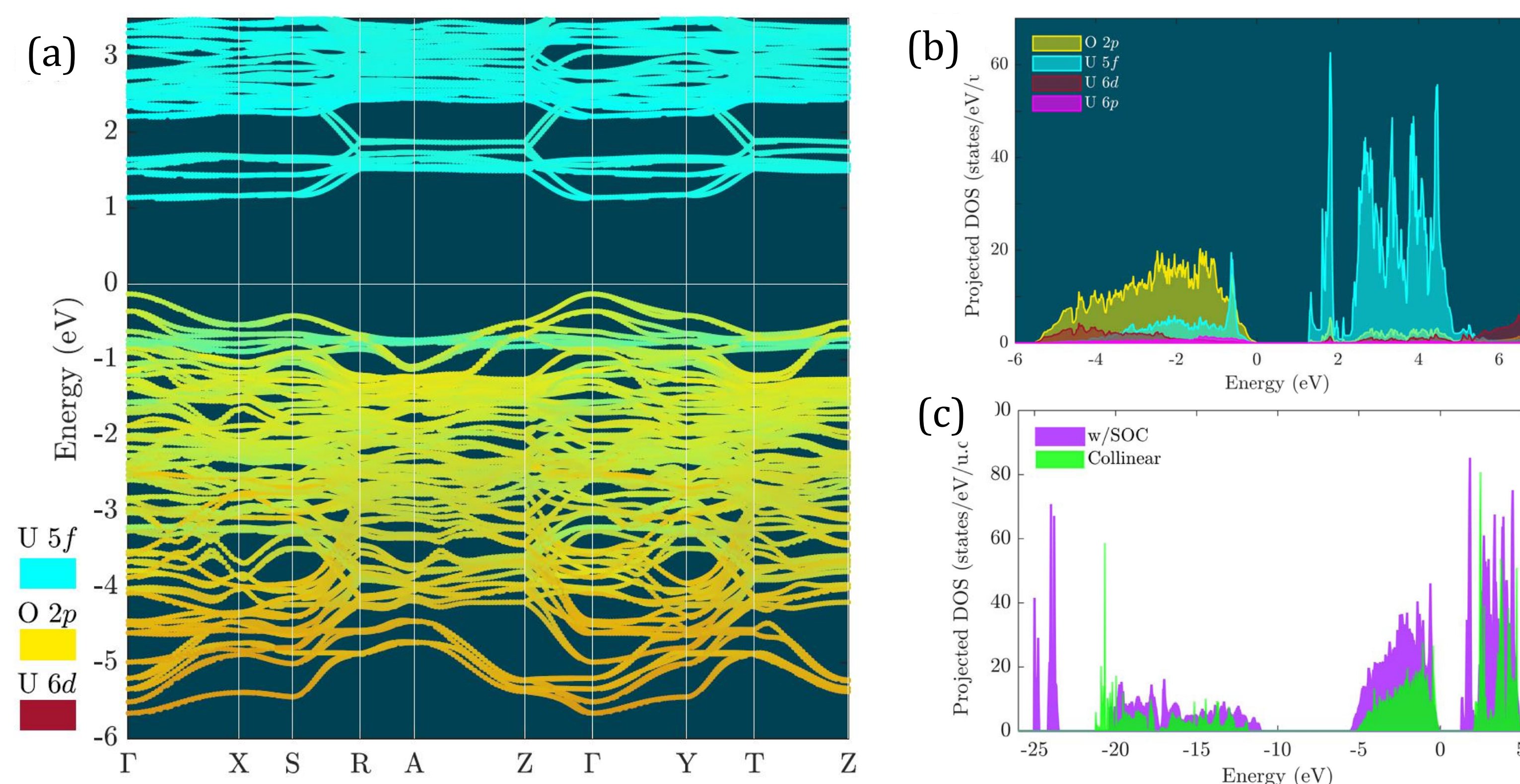
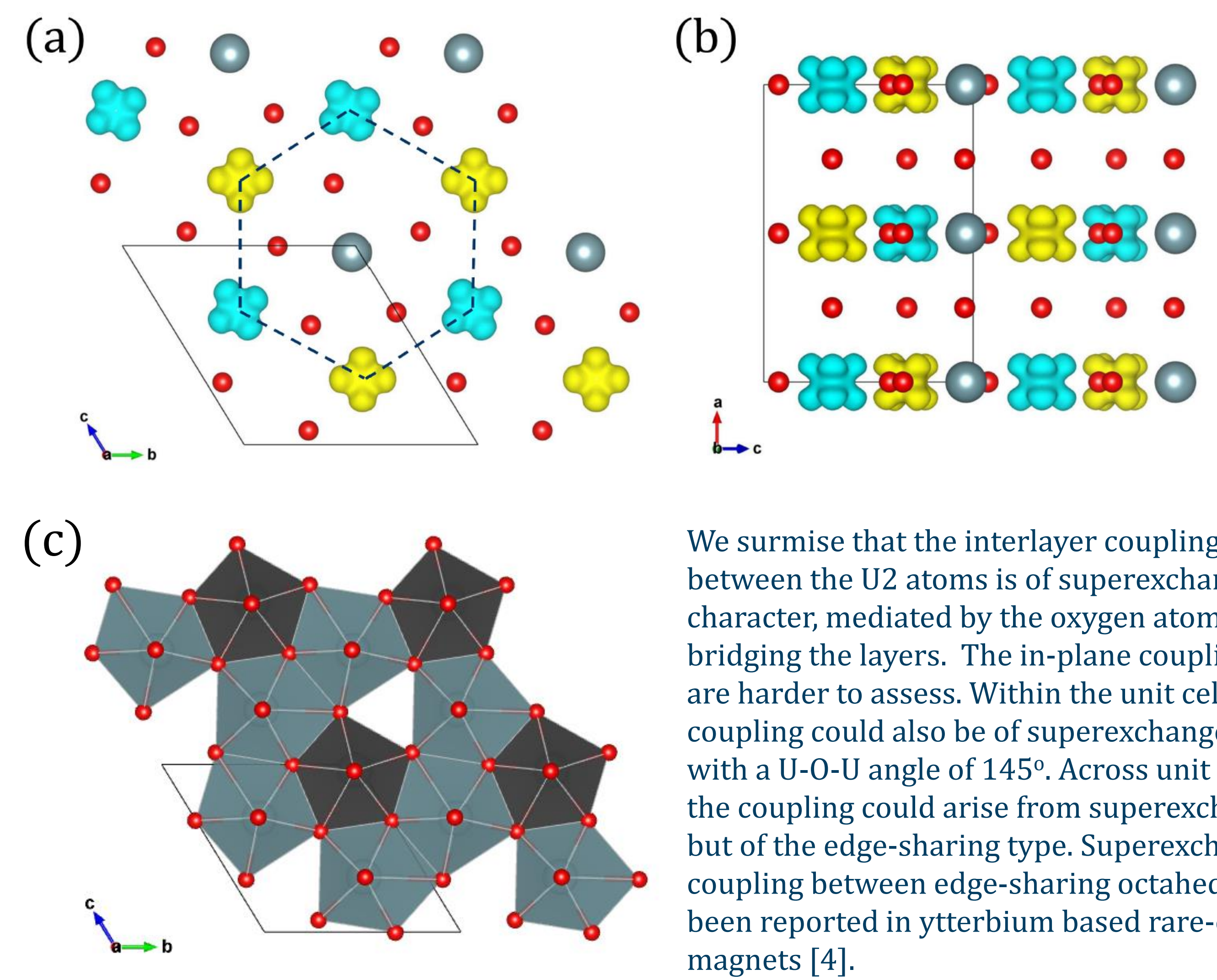


Figure (a) shows the band structure along high symmetry lines in an energy range around the band gap (VBM set at 0). The colors indicate the leading character of the depicted bands. These suggest that  $\text{U}_3\text{O}_8$  is more a charge-transfer semiconductor than a Mott semiconductor. The U 5f states are highly localized, giving rise to the narrow peaks to the projected density of states in Fig. (b). The peak just below the VBM arises from the U2 atoms. The U 5f manifold at the bottom of the conduction band is due to U1 alone. Figure (c) shows the giant effect of SOC on the binding energies, and especially on the conduction band and band gap. With SOC the band gap is 1.27 eV, while without it is 2 eV. On the other hand, we find that without  $U$   $\text{U}_3\text{O}_8$  would be a half metal, with the U2 and U1 5f states nearly degenerate at the bottom of the conduction band.

## Néel type AFM order

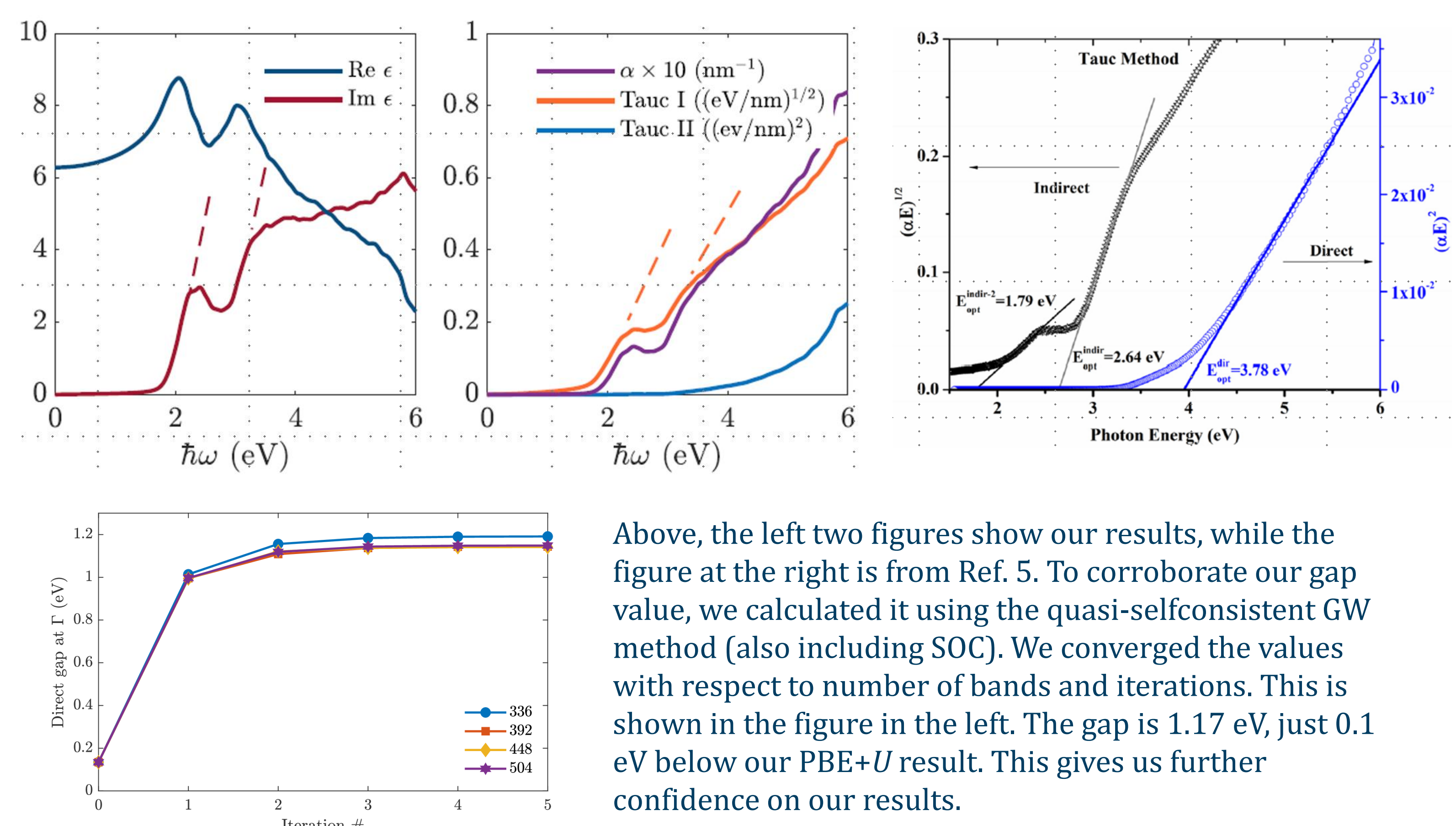
Figure (a) below shows the magnetization density  $m_x(\mathbf{r})$  (the magnetization density in the other directions is zero). The magnetization density of U1 begin zero, the U2 atoms form a slightly distorted Kagomé lattice with Néel type AFM order. The distortion can be associated with the pentagonal distribution of oxygen atoms within a hexagon. The magnetic moment of the U2 atoms is  $0.90 \mu_B$  ( $1.13 \mu_B$  without SOC). Figure (b) shows that the interlayer coupling is AFM as well. Note that the exchange interaction between the U2 atoms is anisotropic. This is best illustrated in Figure (c). Within the unit cell, the pentagonal bi-pyramids of U2a and U2b are corner-sharing, while across unit cell boundaries they are edge-sharing. The bi-pyramid for U1 has a darker color for clarity.



We surmise that the interlayer coupling between the U2 atoms is of superexchange character, mediated by the oxygen atoms bridging the layers. The in-plane couplings are harder to assess. Within the unit cell, the coupling could also be of superexchange type, with a U-O-U angle of  $145^\circ$ . Across unit cells, the coupling could arise from superexchange, but of the edge-sharing type. Superexchange coupling between edge-sharing octahedra has been reported in ytterbium based rare-earth magnets [4].

## Are our calculations correct?

There are no reports on measurements of the U magnetic moments, and measurements related to the electronic structure of  $\text{U}_3\text{O}_8$  are rare. But there is a recent high precision measurement of the optical spectrum [5] (at room temperature) to which we can compare our results. For this we calculated the dielectric function and optical absorption. Convergence with respect of  $\mathbf{k}$ -point mesh and number of bands was ensured at least up to 10 eV. We also calculated the Tauc plots as in Ref. 5 for comparison. The match between the measurements and our results is excellent. Our results show that the optical absorption edge does not correspond to the band gap because the VBM is mainly of p and f character, while the CBM is of f character. Thus, the transitions are not dipole allowed (recall that the conduction bands are very flat). Absorption starts at higher energies, around 2 eV, where the transitions are allowed. This is what experiment is observing. The hump between 2 and 3 eV seen in experiment is also reproduced in our results. It is due to the high peak above the CBM arising from U1 5f states.



Above, the left two figures show our results, while the figure at the right is from Ref. 5. To corroborate our gap value, we calculated it using the quasi-selfconsistent GW method (also including SOC). We converged the values with respect to number of bands and iterations. This is shown in the figure in the left. The gap is 1.17 eV, just 0.1 eV below our PBE+ $U$  result. This gives us further confidence on our results.

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