

**Desmarais *et al.* Reply:** Monteseuro *et al.* [1] (henceforth referred to as “the Comment”) provide an interpretation of pressure-dependent x-ray absorption near-edge structure (XANES) experimental data of EuO, showing an increasing crystal-field splitting (CFS) between the  $5e_g$  and  $5t_{2g}$  subsets of the  $5d$  band, thus confirming the mechanism originally proposed in our previous theoretical study [2] (hereafter referred to as “the Letter”). Let us briefly recall the main steps in the interpretation of the pressure-dependent XANES of EuO.

Since the original report on the high-pressure (HP) behavior of EuO [3], the change in its electronic structure had been interpreted from changes to the Eu oxidation state (OS). This idea was maintained by Souza-Neto *et al.* [4], in their original interpretation of the XANES spectra. The HP XANES data were fitted to a linear combination of the ones from EuO (containing  $\text{Eu}^{2+}$ ) and  $\text{Eu}_2\text{O}_3$  (containing  $\text{Eu}^{3+}$ ) obtained at ambient conditions. From knowledge of the ambient-pressure electronic structures of EuO and  $\text{Eu}_2\text{O}_3$ , an increasing OS would involve a significant charge transfer from the localized  $4f$  to the more delocalized  $5d$  orbital states.

In the Letter, we presented global-hybrid density-functional theory calculations, showing a minor transfer of  $4f$  electrons toward the  $5d$  level (nominally  $0.05e$  from 0 to 33 GPa, see Figs. 1 and S10 of the Letter), followed by an abrupt depopulation of  $5d$  electrons from 33 to 48 GPa. Moreover, the calculations predicted a transfer of  $0.15e$  from the  $5e_g$  subset toward the  $5t_{2g}$  subset from 0 to 48 GPa [Figs. 2(c), and 2(d) of the Letter]. Therefore, the change with pressure in the electronic structure of EuO beyond 33 GPa could not be explained by a change in OS, but rather by an increase in CFS. The key role of increasing CFS in explaining the HP behavior of EuO is stressed in the analysis of orbital populations, the abstract and in the concluding paragraph of the Letter. Indeed, much of the Letter discusses the effect of CFS from the point of view of orbital populations (= the energy integral of the occupied DOSS), whose variations directly reflect an increasing CFS with pressure.

The Letter also showed that the experimental XANES data of Souza-Neto *et al.* are consistent with an increasing CFS with pressure, according to an interpretation based on the dipole-field approximation. Figure 3 of the Letter is a representation of the DOSS of empty  $t_{2g}$  and  $e_g$  levels. It is observed that the density of empty  $e_g$  states increases in intensity and narrows with pressure. At 48 GPa, the  $e_g$  DOSS appears as a discrete peak at a distance of  $\sim 5$  eV from the lowest-energy peak of the  $t_{2g}$  DOSS, which provides an estimate of  $\sim 5$  eV for the CFS of EuO at HP (in remarkable agreement with the new experimental value of 4.9 eV reported by the Comment). What is more, the DOSS data of Fig. 3 of the Letter can be used to quantify the increase in CFS with pressure (even though this was not explicitly discussed in the Letter). This is achieved by taking the difference of the lowest-energy peak in the  $t_{2g}$  DOSS (remaining at 4.7 eV in the three panels of

Fig. 3) and the  $e_g$  one (increasing in energy from 7.5 eV at 10 GPa to 8.8 eV at 48 GPa), yielding an increase in CFS of 1.3 eV with pressure, again in remarkable agreement with the experimental value of  $4.9 - 3.7 = 1.2$  eV (from 4 to 40 GPa) provided in the Comment.

In the Comment, we read “... the  $5d$  orbitals influence in XANES spectra is within the absorption edge...” and “... the FO [first oscillation] does not correspond to the empty  $5e_g$  band.”

However, the  $5d$  DOSS provided in the Comment are only at 0 GPa, while the ones in the Letter are at HP, showing that the empty  $5e_g$  states are shifted to higher energy (because of increasing CFS, see Fig. 3 of the Letter), which confirms that the FO corresponds to the empty  $5e_g$  band.

The confusion perhaps stems from one poorly written sentence of the Letter: “The energy difference between the maxima of the  $t_{2g}$  and  $e_g$  bands is about 5 eV (see blue dashed lines in the figures) and does not change much with pressure.”

The blue dashed lines in Fig. 3 approximate the barycenter (not the maxima) of the empty  $t_{2g}$  and  $e_g$  DOSS. Even though the barycenters are constantly split by around 5 eV, this does not indicate a constant CFS with pressure, as the data instead support an increasing CFS from 3.7 to 5.0 eV, in excellent agreement with the new experimental data of the Comment, as stated above.

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