Comment on "Mechanisms for Pressure-Induced Isostructural Phase Transitions in EuO"

Desmarais *et al.* [1] present a theoretical model that reinterprets the changes observed in the x-ray absorption near edge structure (XANES) spectra of EuO under pressure. They explain the increase of the first oscillation (FO) of the XANES spectra, published by Souza-Neto *et al.* [2], from the abrupt depopulation of $5e_g$ bands. They assign the white line (WL) around 6975 eV to the $5t_{2g}$ bands, and the FO around 6982 eV to the $5e_g$ bands [Fig. 1(a)]. Since the difference of both oscillations remains constant with pressure they provide a practically constant crystal-field splitting (CFS) of 5 eV and interpret their projected densities of states (PDOS) to support it. Their model contradicts two physical theories: (i) CFS has to rise with the cation-ligand distance shortening in a same local environment, and (ii) the $5d$ orbitals influence in XANES spectra is within the absorption edge. The L_3 XANES spectra of lanthanides [Fig. 1(b)] are characterized by a preedge due to the quadrupolar transition from $2p$ to $4f$ (red curve) and a WL (edge) due to the dipolar transition from the $2p_{3/2}$ to $5d_{3/2,5/2}$ empty orbitals (blue curve), which are split into $5t_{2g}$ and $5e_g$ by crystal field [3,4]. This bimodal structure of the WL due to the CFS can be unveiled by the second derivative [4] of the XANES spectra [dotted lines in Figs. 1(a) and 1(c)] since the CFS corresponds to the energy difference between the two minima.

We have calculated the XANES spectra of EuO from PDOS using FEFF code [Fig. 1(b)] and obtained their CFS values up to 48 GPa [Fig. 1(d)]. Such values have been compared by those extracted from experimental XANES spectra [2] [Fig. 1(a)]. We obtain a CFS of 3.2(2) eV at 0 GPa which coincides with that of 3.1 eV measured by optical absorption [5]. EuO has the highest CFS within the EuX (X: O, S, Se, Te) monochalcogenides. The shorter the Eu-X distance, 3.3 (EuTe), 3.09 (EuSe), 2.98 (EuS) and 2.57 (EuO) (Å), the higher the CFS, 1.5 (EuTe), 1.7 (EuSe), 2.2 (EuS), 3.1 (EuO) (eV) [5].

We also demonstrate that the CFS increases as the Eu-O distance shortens within $Fm\bar{3}m$ phase. This rise is well described [line in Fig. 1(d)] by the experimental relationship between the CFS and the cation-ligand distance R as $\text{CFS} = 10Dq \propto R^{-5}$ in oxides and fluorides [6–8]. To obtain the calculated XANES and the $\text{CFS} \propto R^{-5}$ law we used pressure-dependent structural data published elsewhere [9].

We have demonstrated the two misinterpretations performed by Desmarais *et al.* [1]. The CFS in EuO does not remain constant with pressure and the FO does not correspond to the empty $5e_g$ bands. In conclusion, their new model cannot be used to describe the changes observed in the XANES spectra of EuO under compression.

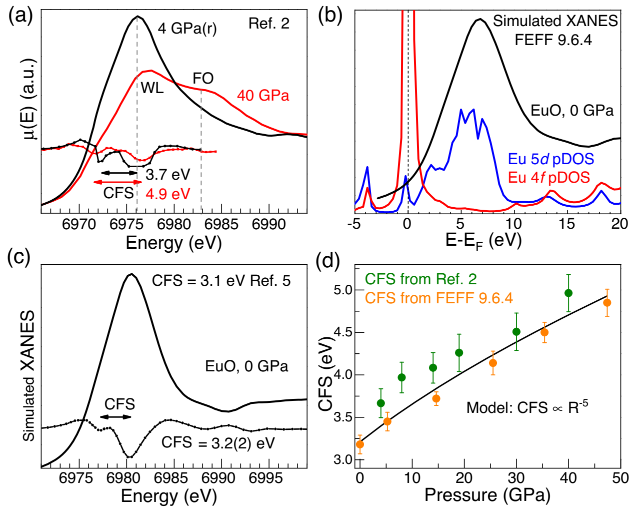

FIG. 1. (a) XANES spectra [2] at 4 GPa (releasing pressure) and 40 GPa with their second derivatives. The gray dash lines mark the WL and FO. (b) Simulated XANES spectrum of EuO at 0 GPa (black) with its Eu $5d$ (blue) and Eu $4f$ (red) PDOS. (c) Simulated XANES spectrum at 0 GPa (line) and its second derivative (dotted line). (d) Pressure dependence of the CFS obtained from our theoretical (orange) and from experimental [2] (green) XANES spectra. Trend of the CFS with R^{-5} law (line).

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[1] J. K. Desmarais, A. Erba, Y. Pan, B. Civalleri, and J. S. Tse, Phys. Rev. Lett. **126**, 196404 (2021).
[2] N. M. Souza-Neto, J. Zhao, E. E. Alp, G. Shen, S. V. Sinogeikin, G. Lapertot, and D. Haskel, Phys. Rev. Lett. **109**, 026403 (2012).

[3] N. M. Souza-Neto, D. Haskel, Y. C. Tseng, and G. Lapertot, Phys. Rev. Lett. **102**, 057206 (2009).

[4] M. A. Laguna-Marco, P. Kayser, J. A. Alonso, M. J. Martínez-Lope, M. van Veenendaal, Y. Choi, and D. Haskel, Phys. Rev. B **91**, 214433 (2015).

[5] G. Busch, G. Güntherodt, and P. Wachter, J. Phys. (Paris), Colloq. **32**, 928 (1971).

[6] R. G. Burns, *Mineralogical Applications of Crystal Field Theory* (Cambridge University Press, Cambridge, England, 1993).

[7] H. G. Drickheimer and C. W. Frank, *Electronic Transitions and the High Pressure Chemistry and Physics of Solids* (Chapman and Hall, London, 1973).

[8] J. A. Barreda-Argüeso, F. Aguado, J. González, R. Valiente, L. Nataf, M. Sanz-Ortiz, and F. Rodriguez, J. Phys. Chem. C **120**, 18788 (2016).

[9] A. Jayaraman, A. K. Singh, A. Chatterjee, and S. Usha Devi, Phys. Rev. B **9**, 2513 (1974).