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

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Desmarais et al. [Phys. Rev. Lett. 126, 196404 (2021)] present a theoretical study of EuO that aims the reinterpretation of the spectral features of its x-ray absorption near edge structure (XANES) spectrum and the pressure dependence of its crystal field splitting (CFS). They assign the $5t_{2g}$ bands to the white line and the $5e_g$ bands to the first oscillation, proposing a constant value of CFS up to 48 GPa. Hence, they contradict the crystal-field theory under pressure and the XANES spectroscopy theory. We present an exhaustive XANES analysis in EuO up to 48 GPa that demonstrates that the proposed model is unsuitable for interpreting its XANES.

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 pre-edge 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 Fig. 1(a) and Fig. 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 CFS = 10 $Dq \propto R^{-5}$ in oxides and fluorides[6–8]. To obtain the calculated XANES and the CFS $\propto R^{-5}$ law we used pressure-dependent structural data published elsewhere[9].

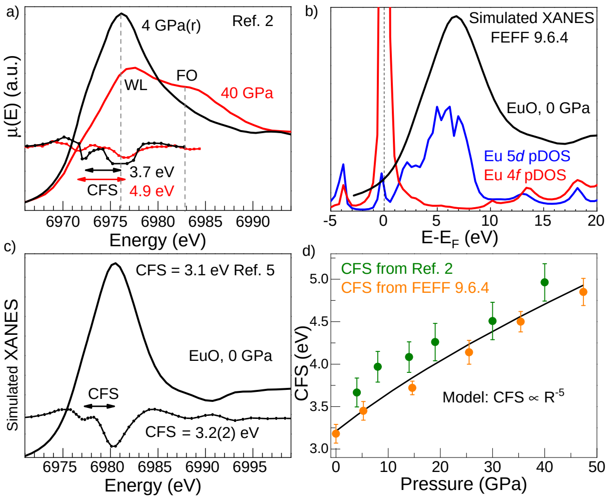

FIG. 1: (a) XANES spectra[2] at 4 GPa (releasing pressure) and 40 GPa with their second derivatives. The grey dash lines mark the WL and FO. (b) Simulated XANES spectrum of EuO at 0 GPa (black) with its Eu $5d$ (blue) and Eu $4f$ (red) pDOS. (c) Simulated XANES spectrum at 0 GPa (line) and its second 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).

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. As a conclusion, their new model cannot be used to describe the changes observed in the XANES spectra of EuO under compression.

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