Electronic Supplementary Information (ESI)

Phonon confinement and interface lattice dynamics of ultrathin high-k rare earth sesquioxide films: the case of Eu_2O_3 on YSZ(001)

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I. Analysis of the XRR data assuming the formation of the EuO layer between the Eu_2O_3 film and the capping layer

In order to check whether the EuO layer, identified by the XANES experiment (Fig. 2(a) of the paper) is located between the Eu_2O_3 film and the Nb capping layer, the XRR data of S1-S4 were fitted assuming the layer configuration depicted as an inset in Fig. S1. The significantly lower quality of the fits (red/solid lines) compared to the model used in the paper (Fig. 2(b) of the paper) strongly suggests that the EuO layer is located between the YSZ(001) substrate and the Eu_2O_3 film.

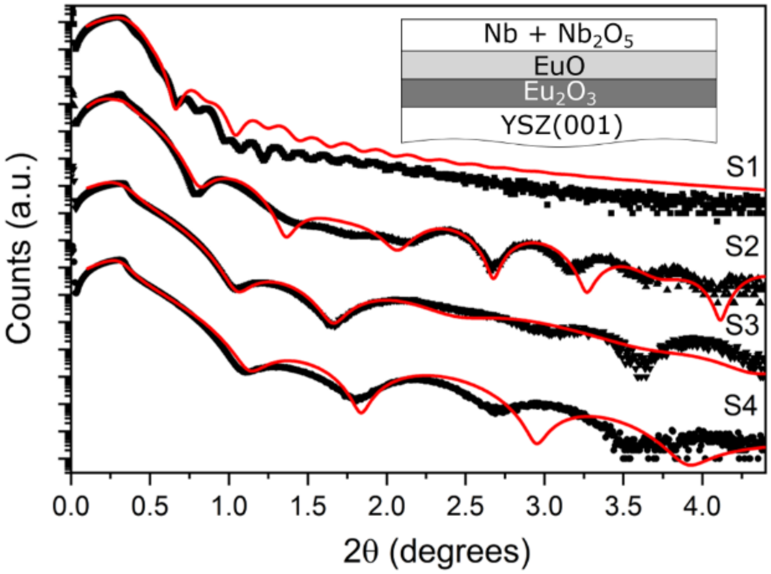

Fig. S1. XRR data of the investigated samples. The red lines stand for the fit assuming the layer sequence depicted in the inset.

II. XRD data of S1-S4

Fig. S2 shows the XRD scans of S1-S4 and the support plate, on which the samples were fixed for the measurements. In addition to the peaks arising from the YSZ(001) substrate and the support plate, Fig. S2 shows a broad feature at ca. 32 deg for S2-S4. In S1 (film thickness of 21.3 nm), this feature transforms into a broad and well-pronounced peak, which corresponds to the (400) reflection of cubic Eu_2O_3 ((800) reflection is also present). The derived lattice constant is 10.80 Å, which is by 0.5% smaller than the bulk value (10.86 Å) [1]. The asymmetric shape of the broad feature at ca. 32 deg in the XRD data of S2-S4 indicates the formation of single crystalline films, which might have epitaxial relationship with the layer below, which is EuO. Epitaxial growth of EuO(001) on YSZ(001) was reported elsewhere [2]. Although the applied growth conditions of the samples (oxygen pressure, temperature of the substrate and annealing time) were deliberately chosen to differ significantly from the optimal conditions for epitaxial growth of EuO on YSZ(001), an epitaxial EuO(001) monolayer might have grown on the YSZ(001) (both materials have perfectly matching lattice constants), due to the limited possibility to control the processes taking place at the interface. The lattice constants of EuO (5.14 Å) and the cubic phase of Eu_2O_3 differ by almost a factor of two. Therefore, it cannot be excluded that at very low thicknesses Eu_2O_3 is stabilized as a single crystalline layer on the EuO monolayer. The additional intensity between 36 and 40 deg in the XRD data of S2-S4 might originate from thickness oscillations, further supporting the assumption of superlattice formation. The XRD scan of S1 does not exhibit thickness oscillations, indicating that the film might be polycrystalline. We note that the crystalline quality of the films was checked immediately after their preparation in the growth chamber by reflection high-energy electron diffraction (RHEED). For none of the samples a diffraction pattern was observed. Most likely, the reason is charging effect due to the insulating nature of the samples.

The investigated Eu_2O_3 and EuO exhibit cubic symmetry, implying that the PDOS is isotropic for both single- and polycrystalline state. Therefore, the applied fitting model of the experimental PDOS (Eq. (1) of the paper) is valid independently from the crystalline state of the samples.

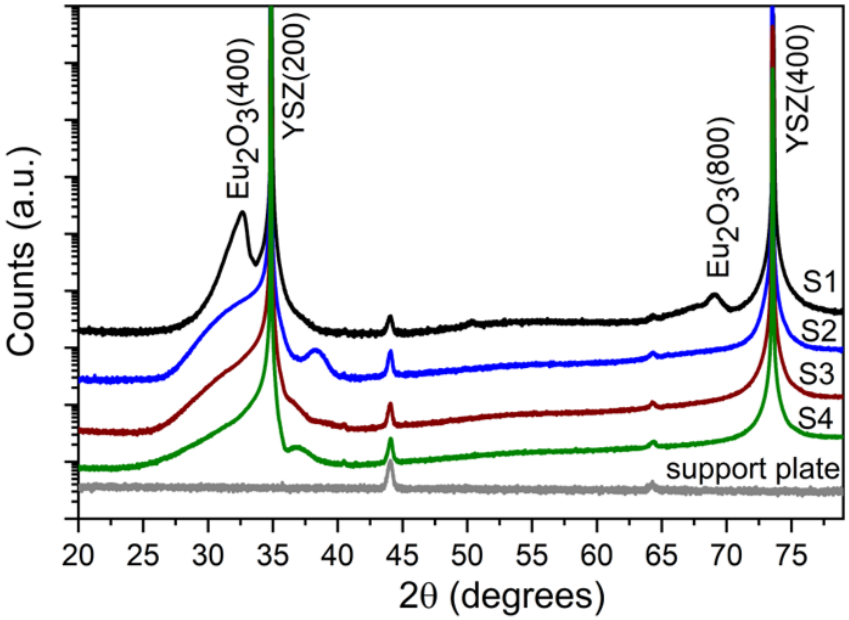

Fig. S2. X-ray diffraction scans of the investigated samples and the support plate.

III. Analysis of the PDOS of S1-S4 with trigonal and monoclinic crystal phases of Eu_2O_3

Eu_2O_3 exists in cubic, trigonal or monoclinic crystal phases. The X-ray diffraction study confirmed that S1 exhibits the cubic phase. For S2-S4, however, there is no direct evidence about their crystal phases. Therefore, we checked if better fits of the experimental PDOS data can be obtained using the Eu-partial PDOS of the other two phases reported elsewhere [1].

Fig. S3 shows the obtained fits using the model described in the paper replacing the Eu-partial PDOS of the cubic phase with the one corresponding to trigonal (left-hand graph) and monoclinic (right-hand graph). Fig. S3 demonstrates that for S1-S3 the PDOS of the cubic crystal phase (reported in Fig. 1(a) of the paper) provides the best modeling of the experimental PDOS data. While this conclusion is not straightforward for S4, a comparison of the fit quality, quantified by the sum of squared residuals, confirms that the best fits also for S4 are obtained by assuming the cubic phase of Eu_2O_3.

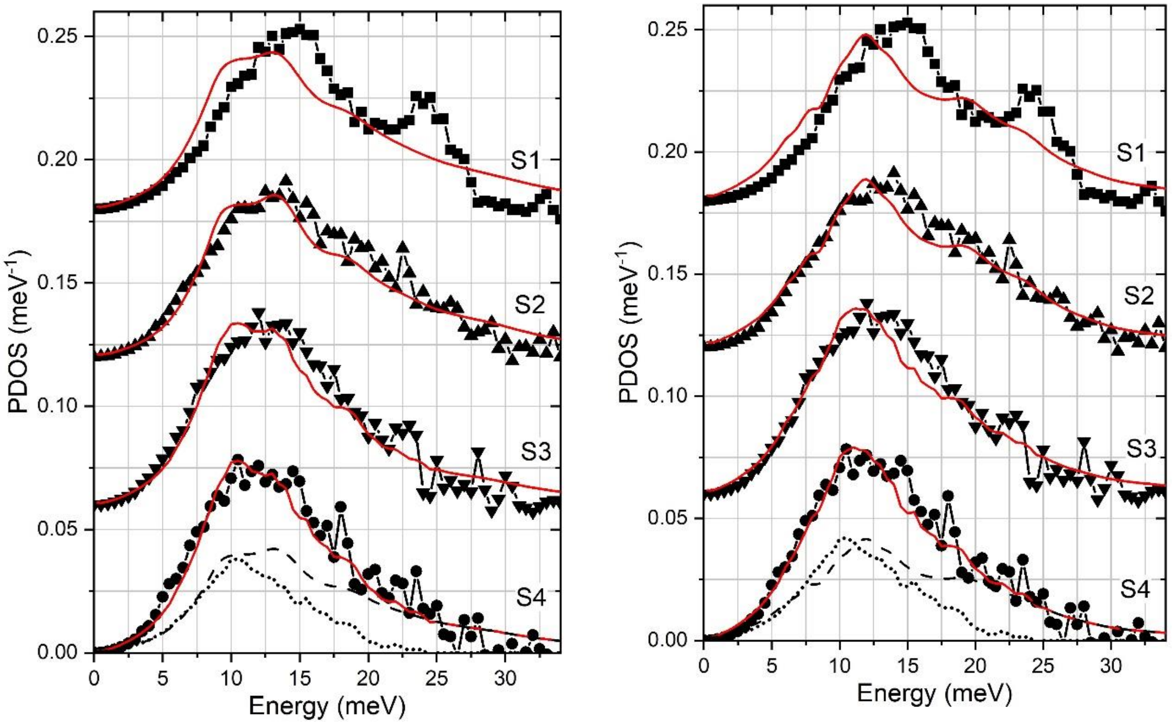

Fig. S3. Fits (red/solid lines) of the experimental PDOS of the investigated samples assuming the trigonal (left) and monoclinic (right) crystal phases of Eu_2O_3 (dashed lines). The dotted lines stand for the Eu-partial PDOS of 2.0 nm thick EuO film [3].

IV. Influence of the Lamb-Mössbauer factors of EuO film and Eu_2O_3 on the analysis approach

From the theory of nuclear inelastic absorption it follows that in the case of coexistence of two or more nonequivalent lattice sites of the Mössbauer-active isotope in the sample, the PDOS is not an additive function [4,5]. This fact arises from the possible difference of the Lamb-Mössbauer (L-M) factor, which is the probability for nuclear resonant absorption/emission of γ-quanta by the nucleus of the two phases. This difference might result in an incorrect subtraction of the multiphonon terms from the experimentally measured spectrum of nuclear inelastic absorption. The lower the L-M factors the bigger the effect is. Unlike the PDOS, however, the spectrum of nuclear inelastic absorption is an additive function upon a proper normalization given by the Limpkin's sum rules [6].

In the data analysis procedure, we fitted the experimental PDOS of the samples with the model:

$$g_{model}(E,Q)=Ag_{if}(E)+(1-A)g_{th}(E,Q)$$

which is a linear combination of $g_{if}(E)$, the PDOS of a 2.0 nm thick EuO film and $g_{th}(E,Q)$, the PDOS of the cubic-phase Eu_2O_3 crystal convoluted with the damped harmonic oscillator function characterized by a quality factor Q. A is the relative fraction of the EuO interface. Q and A were fit parameters. The L-M factors of the EuO film and the Eu_2O_3 crystal at 298 K are 0.3 and 0.6, respectively, which raises the question whether a significant deviation from the real value of A is to be expected due to this difference.

In order to estimate a possible deviation of the parameter A in our modelling approach due to the factor of two difference of the L-M factors of the two phases, we performed the following simulations. We considered three virtual samples consisting of a mixture of EuO and Eu_2O_3, with ratios EuO_{film}:Eu_2O_3 of 0.25:0.75, 0.5:0.5 and 0.75:0.25. For each of these samples we composed the PDOS as a linear combination of the PDOS of both phases following the respective ratios, hereinafter referred to as *approach A*. The results are plotted with black line in Fig. S4. In *approach B*, we composed the normalized spectra of nuclear inelastic absorption according to these ratios. From these spectra we calculated the PDOS of the three virtual samples. The results are plotted with blue line in Fig. S4. A direct comparison of the PDOS obtained by these two approaches reveals minor differences between them. Therefore, we conclude that the impact of the different L-M factors of the two oxide phases on the modelling approach is negligible. This assumption is further supported by the fact that the obtained values of A are qualitatively consistent with the results derived by XRR and XANES (see Table 1 of the paper).

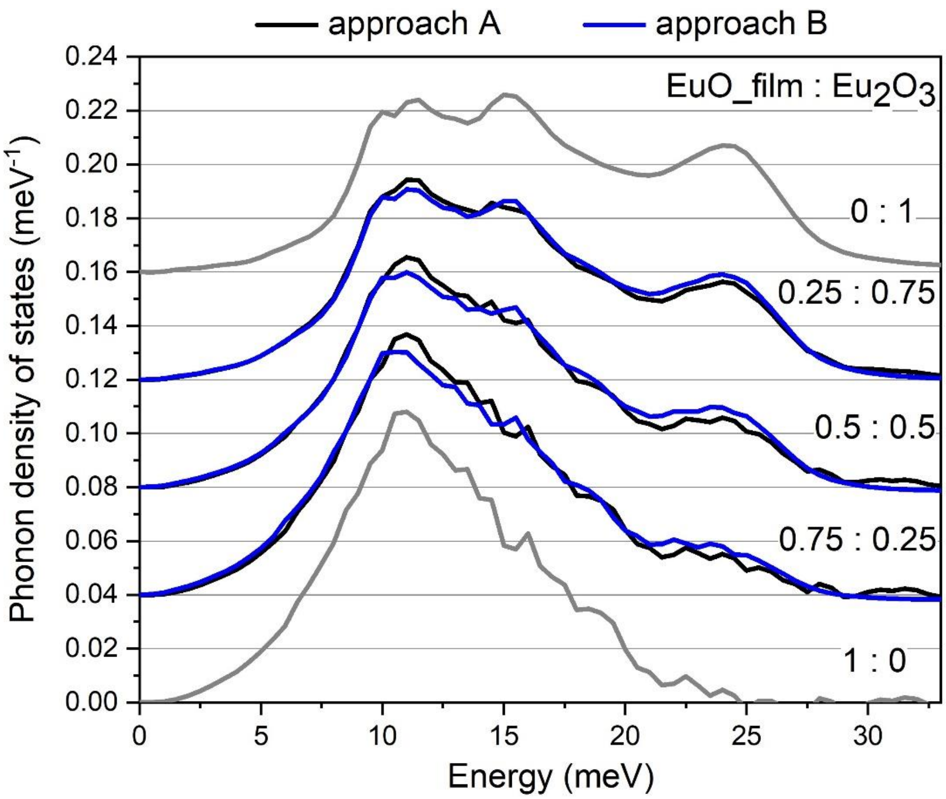

Fig. S4. Eu-partial PDOS of the cubic phase of Eu_2O_3 (convoluted with the damped harmonic oscillator with Q=12) [1] and of 2.0 nm thick EuO film [3] along with the corresponding ratios calculated by the approaches explained in the text.

References:

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