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Reentrant valence transition in EuO at high pressures: beyond the bond-valence model

N. M. Souza-Neto,^{1,2,*} J. Zhao,¹ E. E. Alp,¹ G. Shen,³ S. V. Sinogeikin,³ G. Lapertot,⁴ and D. Haskel^{1,†}

¹*Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, U.S.A.*

²*Laboratório Nacional de Luz Síncrotron, Campinas, SP 13083-970, Brazil*

³*HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, U.S.A.*

⁴*SPSMS, UMR-E 9001, CEA-INAC/UJF-Grenoble 1, 17 rue des martyrs, 38054 Grenoble, France*

The pressure-dependent relation between Eu valence and lattice structure in model compound EuO is studied with synchrotron-based x-ray spectroscopic and diffraction techniques. Contrary to expectation, a 7% volume collapse at ≈ 45 GPa is accompanied by a reentrant Eu valence transition into a *lower* valence state. In addition to highlighting the need for probing both structure and electronic states directly when valence information is sought in mixed-valent systems, the results also show that widely used bond-valence methods fail to quantitatively describe the complex electronic valence behavior of EuO under pressure.

The phenomenon of mixed-valency in f -electron systems occurs when otherwise localized f -orbitals of Rare-Earth or Actinide elements hybridize in the solid with s, p, d electrons. A quantum superposition of differently occupied (valence) f -states emerges when the energy difference between competing single-valent states is smaller than the f -electron bandwidth, usually termed fluctuating valence state [1]. The onset of mixed-valency under applied pressure, chemical substitutions, or finite temperature has dramatic consequences on the macroscopic properties of f -electron systems including volume collapse [2], quenched magnetism [3], onset of superconductivity [4, 5], Kondo physics [6], and quantum criticality [4, 5]. Despite mixed-valency being central to f -electron physics, our ability to directly probe this peculiar quantum electronic state at high pressures is limited.

EuO with its simple NaCl (B1) crystal structure is a model system to study valence effects upon lattice compression [7]. Eu-containing compounds are prototypical mixed-valent systems because Eu can display both trivalent (as most Rare-Earths ions do) and divalent electronic states at ambient conditions, the latter stabilized by a half-filled $4f$ orbital occupation ($[\text{Xe}]4f^7 5d^0 6s^2$ configuration) [1]. Additionally, the ferromagnetic-semiconductor character of EuO [7] coupled with perfect spin-polarization of electronic states near the Fermi level generated interest for possible applications of EuO in Spintronics [8]. A dramatic, three-fold increase in magnetic ordering temperature is observed under applied pressures of up to ≈ 14 GPa (or at strained interfaces), reaching a maximum $T_C \approx 200$ K but decreasing at higher pressures [9]. The relationship between crystal structure, electronic structure and magnetic ordering temperature has fueled much of the research in EuO over the last two decades, with the question of Eu valency remaining key for a complete understanding of this and other f -electron mixed-valent systems. In this *Letter* we report direct measurements of electronic valence and crystal structure in Europium monoxide (EuO)

at pressures up to 90 GPa using x-ray absorption spectroscopy, nuclear forward scattering and x-ray diffraction techniques. Below 40 GPa a complex, pressure-dependent valence is observed to fluctuate between Eu^{2+} and Eu^{3+} states at a frequency $f \gtrsim \Delta E/\hbar \sim 0.15$ Peta-Hertz where ΔE is the $4f$ bandwidth. At higher pressures we observe a novel reentrant valence transition in Eu ions into a lower valence state despite a concomitant 7% volume collapse. Oftentimes, valence state is derived from structural data alone via bond valence sum rules [10–12], which relate interatomic distances and coordination number to valence. We demonstrate that bond-valence models fail to quantitatively describe the pressure-dependent mixed-valent states of EuO in a broad pressure range. The results call for revisiting the vast literature on mixed-valent f -electron systems where electronic valence is inferred from structural data alone.

Polycrystalline samples of EuO were prepared as described in ref [13]. X-ray diffraction (XRD), x-ray absorption near-edge spectroscopy (XANES) and nuclear forward scattering (NFS) experiments under pressure were performed at beamlines 16-BM-D, 4-ID-D and 3-ID-D of the Advanced Photon Source, Argonne National Laboratory, respectively. Sample loading into the diamond anvil cell was carefully done in an Argon atmosphere to prevent oxidation. Pressure was calibrated *in situ* by the Ruby luminescence method [14]. Additional details of the experimental methods are presented below and in the supplemental material [15].

In view of the limited pressure range of previous studies, together with conflicting reports on the pressure dependence of its lattice parameter [10, 16], we carried out high-precision XRD measurements to determine the pressure-volume relation in EuO up to 92 GPa (Fig. 1). We used Neon as pressure-transmitting medium and diffraction peaks from reference Gold particles for *in-situ* pressure calibration. A very modest volume collapse ($\approx 0.5\%$) occurs at ≈ 35 GPa with no change in crystal structure (NaCl- B1), likely related to electronic insta-

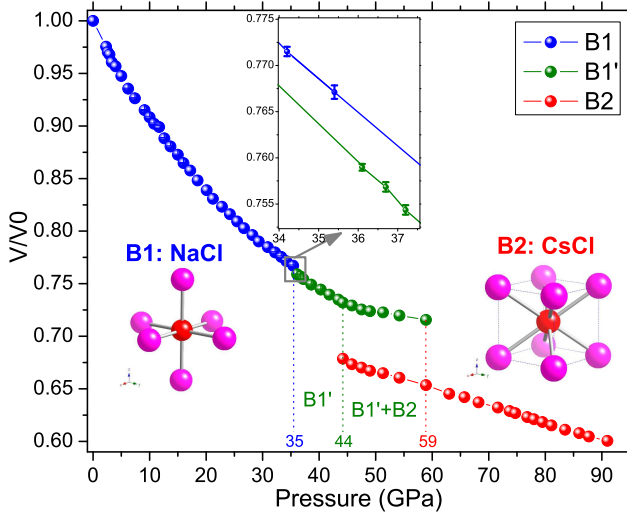


Figure 1: Pressure-volume dependence of EuO up to 92 GPa obtained from Rietveld refinements of XRD data. The inset panel shows a modest iso-structural volume collapse at about 35 GPa (B1' phase). From 44 to 59 GPa a mixture of NaCl (B1) and CsCl (B2) phases is present. Above 59 GPa a CsCl structural phase is homogeneous over the sample volume. Two schematic figures show the local coordination in NaCl and CsCl phases.

bilities as interpreted by Jayaraman *et al.* [10]. Starting at about 44 GPa a first-order structural transition to a CsCl (B2) structure takes place with detectable coexistence of both phases over the sample volume up to 59 GPa, in fair agreement with a previous report [16]. After reaching about 92 GPa, the pressure was released and the structural changes were observed to be reversible. XRD results were previously used to argue, based on bond-valence sum rules [11, 12], that the valence of Eu in EuO dramatically increases as a function of pressure with a first order valence transition towards a Eu^{3+} state taking place at the modest isostructural volume collapse resulting in a 2.5+ valence at about 35 GPa [10, 17]. While a volume collapse could in principle be a signature of a sizable increase in valence, just the opposite takes place at the structural phase transition in EuO, as discussed below.

XANES data were collected in order to directly probe the electronic structure of EuO as a function of lattice contraction. A previous report [18] provides evidence for a direct correlation between Eu $4f$ - $5d$ electronic mixing and the increase in ferromagnetic ordering temperature that takes place in EuO up to ≈ 14 GPa. Despite the presence of f - d mixing no evidence of mixed valency was found in this pressure regime where a stable, fractional (non-integer) occupation of $4f$ orbitals is found instead. The difference in excitation threshold for a $2p_{3/2} \rightarrow 5d$ electronic transition (Eu L_3 absorption edge) in $4f^7 5d^0$ (Eu^{2+}) and $4f^6 5d^1$ (Eu^{3+}) configurations is ≈ 8.0 eV, as shown in Fig. 2. While standards with known valence

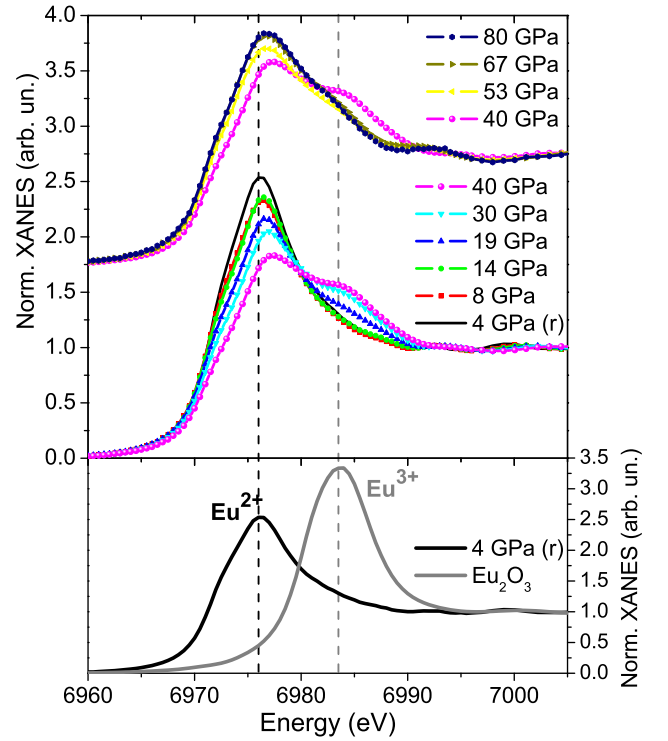


Figure 2: Eu L_3 XANES measurements on EuO up to 80 GPa. The bottom panel compares spectra for Eu^{2+} and Eu^{3+} ions in EuO and Eu_2O_3 , respectively. An ≈ 8 eV threshold energy difference unequivocally distinguishes the two valence states. The top panel shows XANES spectra in the 4 to 40 GPa pressure range where fractional [$P < 14$ GPa] and mixed valence [$14 < P < 40$ GPa] states are observed, with translated spectra showing the reentrant valence behavior at higher pressures [45-60 GPa] coincident with the volume collapse transition. The 4 GPa spectrum was taken upon pressure release indicating reversibility of the electronic transition.

state, such as Eu_2O_3 , can be used to determine the degree of mixed valency an accurate estimate must also consider the effects of crystal structure upon the XANES spectra [28]. Between 14 and 40 GPa Eu is found to be in a mixed valence state, reaching 2.21+ at 40 GPa. The fractional $4f$ occupancy below ≈ 14 GPa, and the degree of mixed valency above this pressure agree well with previous work [9, 17, 19, 20] where the valence of Eu was explored in the context of transport and magnetic properties. The appearance of mixed valency appears to coincide with the downturn in ferromagnetic ordering temperature [9], a result of an increased fraction of $J = |L + S| \approx 0$ Eu^{3+} ions. Remarkably, at higher pressures a *lower* valence state is abruptly recovered concomitant with the $\text{B1} \rightarrow \text{B2}$ structural phase transition; i.e., the $\approx 7\%$ volume collapse is accompanied by a *decrease* in Eu valence. An increase in Eu-O bond length in the high-pressure B2 phase as a result of the change in Eu coordination number from $N=6$ (NaCl) to $N=8$ (CsCl) allows for the reentrant valence transition to occur despite the sizable macroscopic

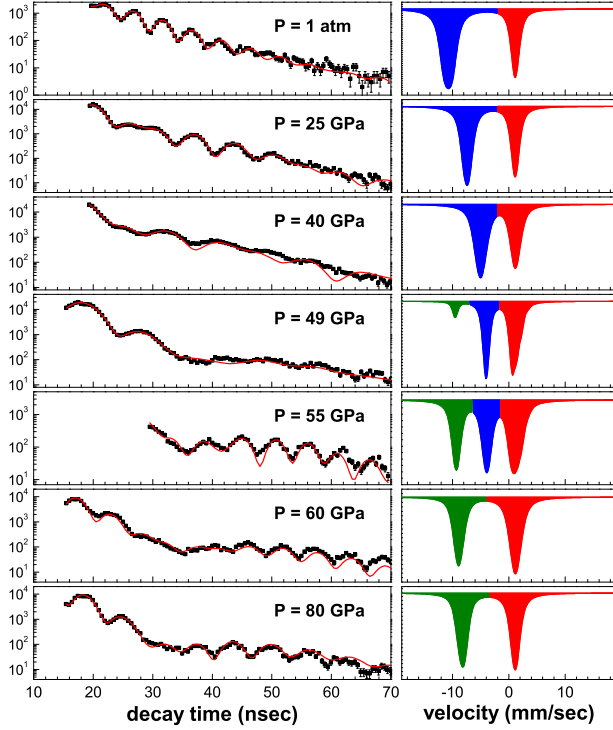


Figure 3: Synchrotron Mössbauer spectra of EuO under pressure, collected using an Eu_2O_3 sample at ambient pressure as reference, are shown in the time domain in the left panel together with fits to the data. Fit results were used to simulate spectra in the energy domain shown in the right panel. Red peaks correspond to the Eu_2O_3 reference located after the diamond anvil cell, blue peaks correspond to the B1 phase of EuO, and green peaks to the B2 phase. A complete dataset for all pressures is given with the supplemental material [15].

volume contraction.

The pressure dependence of the Eu valence was verified with the NFS technique [21], which probes valence through the Mössbauer isomer-shift (IS), namely, the change in s -electron density at the nucleus of a Mössbauer isotope as a result of changes in $4f$ electron occupation [1, 22]. An accurate description of valence from NFS requires taking into account the compression of s -like wave functions induced by lattice contraction [22, 23], unrelated to changes in valence (see supplemental material [15] for details). The NFS data in Fig. 3 indicate that the Eu^{2+} valence changes towards Eu^{3+} below 50 GPa, in fair agreement with previously reported Mössbauer data [23] [29]. At pressures above the structural phase transition, however, a near Eu^{2+} state is recovered in good agreement with the XANES. Moreover, the presence of a single resonance in the Mössbauer spectra unequivocally demonstrates that the compound displays a spatially homogeneous Eu valence (i.e. all Eu sites are equivalent) below and above the structural phase transition. The exception is the region of phase coexistence between 44 and 59 GPa where the appearance of a sec-

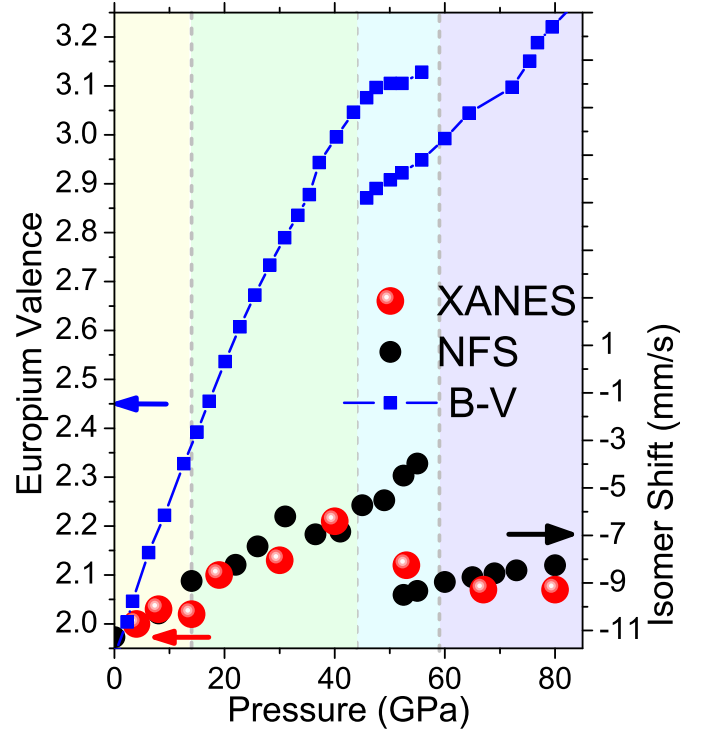


Figure 4: Europium valence determined by XANES, NFS and bond-valence-parameterization is shown in the left axis. The IS determined by NFS is shown in the right axis. Valence from NFS is obtained after volume correction based on the B1 phase compressibility [23]. XANES and NFS results are in good agreement, but at odds with the bond-valence-parameterization method. Colors differentiate the four different valence regimes as described in the text.

ond resonance is indicative of a spatially inhomogeneous Eu valence.

While XANES spectra discretely present both Eu^{2+} and Eu^{3+} valence states at each pressure, the Mössbauer IS from NFS shows a single, intermediate valence between Eu^{2+} and Eu^{3+} states. This is understood based on the different time scales of XANES and NFS experiments. The probing time of about fifty attosec (core-hole lifetime of 5×10^{-17} sec) in XANES spectroscopy at the Eu L_3 absorption edge (6.97 keV) is much faster than the 1.4×10^{-8} sec lifetime of the ^{151}Eu nuclear excited state [24]. While a mixed-valence state can be expressed as a superposition of $4f^7$ and $4f^6$ wavefunctions at a given instant, fluctuating valence states are present due to the characteristic frequency defined by the non-zero $4f$ bandwidth [1]. At ambient pressure a bandwidth of about 0.1 eV corresponds to a valence lifetime of $\approx 6 \times 10^{-15}$ sec. Consequently, the Mössbauer experiment sees a fast fluctuating valence [1] as a static average of both states while the XANES process is fast enough to separately probe both states. Interestingly, the proximity in the lifetime of the fluctuating valence state and lattice fluctuations ($\approx 10^{-13}$) may influence how the magnetism

[9, 18, 19, 23, 25] and conductivity [17, 25, 26] of EuO respond to pressure as the $4f$ electronic bandwidth changes with lattice contraction.

The general approximation “bond length is a unique function of bond valence” [11] is widely used to determine a material’s valence based on crystal structure. The prediction of valence by these methods [1, 10–12] is done using a linear combination of lattice constants as a function of pressure considering the ionic radius of, for example, Eu^{2+} and Eu^{3+} ions (which differ by about 10%). We used the parameterization method of [11] to calculate the valence based on bond distances from XRD data (see supplemental material [15] for details). The values of valences for EuO as a function of lattice parameter are shown in Fig. 4, where we compare the valence determined by this bond-valence parameterization [11] with results from XANES and NFS experiments. It is clear that the over simplifications of the bond-valence method [11], which determines valence based solely on atomic structure, give rise to inaccurate results. For example, any nonlinear dependence of volume on valence, together with changes in the degree of ionicity, would undermine the accuracy of this method [1].

In summary, we have shown that EuO presents four pressure regimes related to fractional and mixed-valent behaviors, which are highlighted here due to their important connection with the magnetic and transport properties under pressure. Below 14 GPa a well-defined quantum state of fractional $4f$ (and $5d$) occupation evolves with pressure, resulting in a continuous increase in magnetic ordering temperature [18]. Between 14 and 44 GPa the Europium atoms display a mixed-valent state composed of discrete Eu^{2+} and Eu^{3+} states, homogeneously distributed over volume and fluctuating with a characteristic frequency determined by the $4f$ bandwidth ($f \gtrsim 0.15$ PHz). This leads to a continuous decrease in magnetic ordering temperature as a result of the $J \approx 0$ state of Eu^{3+} ions. From 44 GPa to 59 GPa, coexistence of NaCl and CsCl structures results in a spatially inhomogeneous valence state, the CsCl structure displaying a reentrant, nearly Eu^{2+} , valence state which becomes spatially homogeneous above 59 GPa. It remains to be seen if the reentrant valence transition is associated with a strengthening of magnetic interactions in EuO at high pressures, interactions that were otherwise weakened by the mixed-valent state [9, 19]. Most importantly we show that widely used bond-valence methods fail to quantitatively describe essential features of the complex electronic valence behavior of EuO under pressure. This highlights the need for probing both structure and electronic states directly when valence information is sought in mixed-valent systems.

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* Electronic address: narcizo.souza@lnls.br

† Electronic address: haskel@aps.anl.gov

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- [29] Note that the correspondence between IS and valence in figure S5b of [15] is only directly applicable when both sample and reference are at ambient pressure.