

## Reentrant Valence Transition in EuO at High Pressures: Beyond the Bond-Valence Model

N. M. Souza-Neto,<sup>1,2,\*</sup> J. Zhao,<sup>1</sup> E. E. Alp,<sup>1</sup> G. Shen,<sup>3</sup> S. V. Sinogeikin,<sup>3</sup> G. Lapertot,<sup>4</sup> and D. Haskel<sup>1,†</sup>

<sup>1</sup>Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

<sup>2</sup>Laboratório Nacional de Luz Síncrotron, Campinas, Sao Paulo 13083-970, Brazil

<sup>3</sup>HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C., USA

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

(Received 12 April 2012; published 12 July 2012)

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  $\approx 45$  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.

DOI: [10.1103/PhysRevLett.109.026403](https://doi.org/10.1103/PhysRevLett.109.026403)

PACS numbers: 71.28.+d, 75.20.Hr

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-earth ions do) and divalent electronic states at ambient conditions, the latter stabilized by a half-filled  $4f$  orbital occupation ( $[\text{Xe}]4f^75d^06s^2$  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  $\approx 14$  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  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  states at a frequency  $f \geq \Delta E/\hbar \sim 0.15$  petahertz, where  $\Delta E$  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 beam lines 16-BM-D, 4-ID-D, and 3-ID-D, respectively, of the Advanced Photon Source, Argonne National Laboratory. 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 ( $\approx 0.5\%$ )

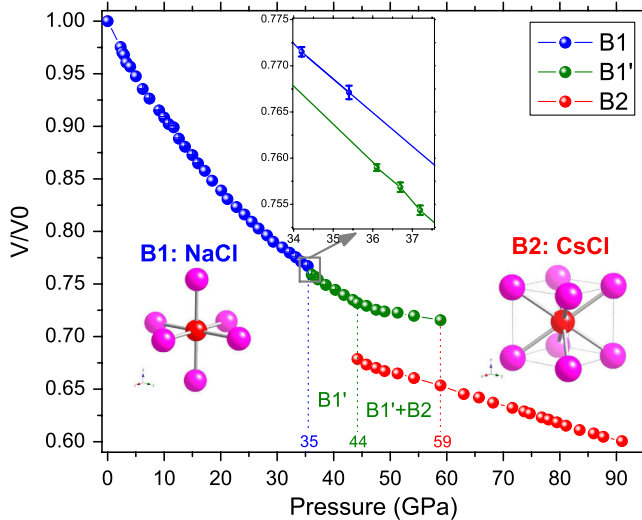


FIG. 1 (color online). Pressure-volume dependence of EuO up to 92 GPa obtained from Rietveld refinements of XRD data. The inset panel shows a modest iso-structural volume collapse at about 35 GPa ( $B1$  phase). From 44 to 59 GPa a mixture of NaCl ( $B1$ ) and CsCl ( $B2$ ) phases is present. Above 59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

occurs at  $\approx 35$  GPa with no change in crystal structure (NaCl- $B1$ ), likely related to electronic instabilities 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  $\text{Eu}^{3+}$  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  $\approx 14$  GPa. Despite the presence of  $f$ - $d$  mixing, no evidence of mixed valency was found in this pressure regime where a stable, fractional (noninteger) 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  $4f^7 5d^0$  ( $\text{Eu}^{2+}$ ) and  $4f^6 5d^1$  ( $\text{Eu}^{3+}$ ) configurations is  $\approx 8.0$  eV, as shown in Fig. 2. While standards with known valence state, such as  $\text{Eu}_2\text{O}_3$ , can be used to determine the degree of mixed valency, an

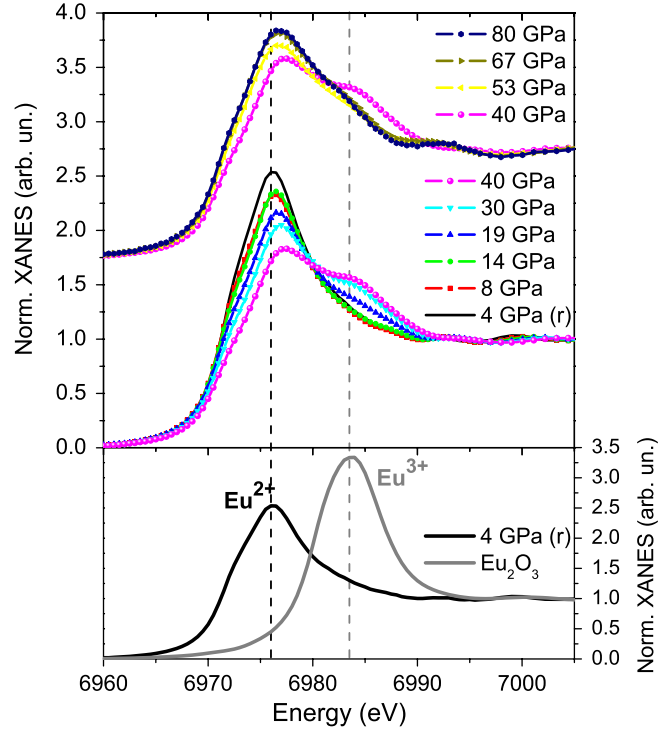


FIG. 2 (color online). Eu  $L_3$  XANES measurements on EuO up to 80 GPa. The bottom panel compares spectra for  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions in EuO and  $\text{Eu}_2\text{O}_3$ , respectively. An  $\approx 8$  eV threshold energy difference unequivocally distinguishes the two valence 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.

accurate estimate must also consider the effects of crystal structure upon the XANES spectra [19]. 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  $\approx 14$  GPa, and the degree of mixed valency above this pressure agree well with previous work [9,17,21,22], 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  $J = |L + S| \approx 0$   $\text{Eu}^{3+}$  ions. Remarkably, at higher pressures a lower valence state is abruptly recovered concomitant with the  $B1 \rightarrow B2$  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 volume contraction.

The pressure dependence of the Eu valence was verified with the NFS technique [23], 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 [1,24]. An accurate description of valence from NFS requires taking into account the compression of  $s$ -like wave functions induced by lattice contraction [24,25], unrelated to changes in valence (see Supplemental Material [15] for details). The NFS data in Fig. 3 indicate that the  $\text{Eu}^{2+}$  valence changes toward  $\text{Eu}^{3+}$  below 50 GPa, in fair agreement with previously reported Mössbauer data [25,26]. At pressures above the structural phase transition, however, a near  $\text{Eu}^{2+}$  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 second resonance is indicative of a spatially inhomogeneous Eu valence.

While XANES spectra discretely present both  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  valence states at each pressure, the Mössbauer IS from NFS shows a single, intermediate valence between  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  states. This is understood based on the different time scales of XANES and NFS experiments. The probing

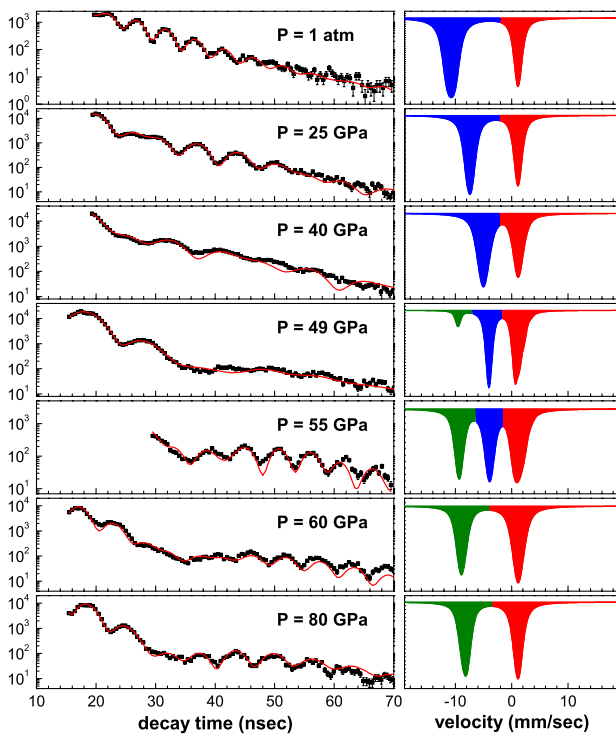


FIG. 3 (color online). Synchrotron Mössbauer spectra of  $\text{EuO}$  under pressure, collected using an  $\text{Eu}_2\text{O}_3$  sample at ambient pressure as reference, are shown in the time domain in the left panel together with fits to the data. Fit results were used to simulate spectra in the energy domain shown in the right panel. Red peaks correspond to the  $\text{Eu}_2\text{O}_3$  reference located after the diamond anvil cell, blue peaks correspond to the  $B1$  phase of  $\text{EuO}$ , and green peaks to the  $B2$  phase. A complete data set for all pressures is given with the Supplemental Material [15].

time of about 50 attosec (core-hole lifetime of  $5 \times 10^{-17}$  sec) in XANES spectroscopy at the  $\text{Eu } L_3$  absorption edge (6.97 keV) is much faster than the  $1.4 \times 10^{-8}$  sec lifetime of the  $^{151}\text{Eu}$  nuclear excited state [27]. While a mixed-valence state can be expressed as a superposition of  $4f^7$  and  $4f^6$  wave functions at a given instant, fluctuating valence states are present due to the characteristic frequency defined by the nonzero  $4f$  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 [9,18,22,25,28] and conductivity [17,28,29] of  $\text{EuO}$  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,  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions (which differ by about 10%). We used the parametrization 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  $\text{EuO}$  as a function of lattice parameter are shown in Fig. 4, where we compare the valence determined

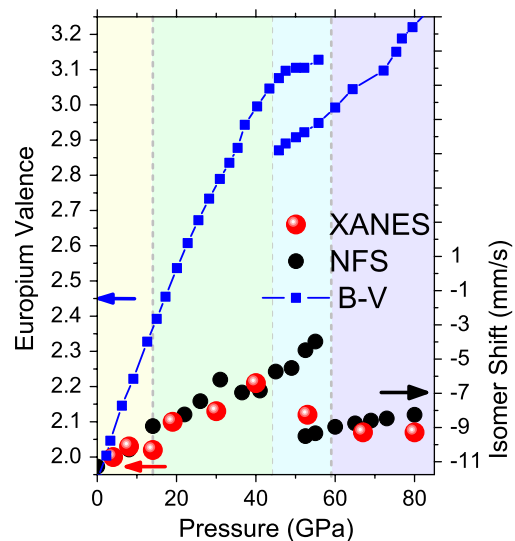


FIG. 4 (color online). Europium valence determined by XANES, NFS, and bond-valence-parametrization is shown in the left axis. The IS determined by NFS is shown in the right axis. Valence from NFS is obtained after volume correction based on the  $B1$  phase compressibility [25]. XANES and NFS results are in good agreement but at odds with the bond-valence-parametrization method. Colors differentiate the four different valence regimes as described in the text.

by this bond-valence parametrization [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  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  states, homogeneously distributed over volume and fluctuating with a characteristic frequency determined by the  $4f$  bandwidth ( $f \geq 0.15$  PHz). This leads to a continuous decrease in magnetic ordering temperature as a result of the  $J \approx 0$  state of  $\text{Eu}^{3+}$  ions. From 44 to 59 GPa, coexistence of NaCl and CsCl structures results in a spatially inhomogeneous valence state, the CsCl structure displaying a reentrant, nearly  $\text{Eu}^{2+}$ , 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 [9,22]. 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.

We are grateful to James S. Schilling and Yves Petroff for commenting on the manuscript. Work at Argonne is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC-02-06CH11357. HPCAT is supported by CIW, CDAC, UNLV, and LLNL through funding from DOE-NNSA, DOE-BES, and NSF. We thank Abdel Alsmadi for help with the NFS measurements.

\*narcizo.souza@lnls.br

†haskel@aps.anl.gov

- [1] C. Varma, *Rev. Mod. Phys.* **48**, 219 (1976).
- [2] J. Arvanitidis, K. Papagelis, S. Margadonna, K. Prassides, and A. Fitch, *Nature (London)* **425**, 599 (2003).
- [3] M. M. Abd-Elmeguid, C. Sauer, and W. Zinn, *Phys. Rev. Lett.* **55**, 2467 (1985).
- [4] Y. Matsumoto, S. Nakatsuji, K. Kuga, Y. Karaki, N. Horie, Y. Shimura, T. Sakakibara, A. H. Nevidomskyy, and P. Coleman, *Science* **331**, 316 (2011).
- [5] M. Okawa *et al.*, *Phys. Rev. Lett.* **104**, 247201 (2010).
- [6] M. Dzero, M.R. Norman, I. Paul, C. Pepin, and J. Schmalian, *Phys. Rev. Lett.* **97**, 185701 (2006).
- [7] P. Wachter, *Handbook on the Physics and Chemistry of Rare Earths* (North-Holland, Amsterdam, 1979), Vol. 2, p. 507.
- [8] A. Schmehl, V. Vaithyanathan, A. Herrnberger, S. Thiel, C. Richter, M. Liberati, T. Heeg, M. Roeckerath, L.F. Kourkoutis, and S. Muehlbauer *et al.*, *Nature Mater.* **6**, 882 (2007).
- [9] V. Tissen and E. Ponyatovskii, *JETP Lett.* **46**, 361 (1987).
- [10] A. Jayaraman, A. Singh, A. Chatterj, and S. Devi, *Phys. Rev. B* **9**, 2513 (1974).
- [11] N. Brese and M. O’Keeffe, *Acta Crystallogr. Sect. B* **47**, 192 (1991).
- [12] I. Brown and D. Altermatt, *Acta Crystallogr. Sect. B* **41**, 244 (1985).
- [13] A. Mauger and C. Godart, *Phys. Rep.* **141**, 51 (1986).
- [14] K. Syassen, *High Press. Res.* **28**, 75 (2008).
- [15] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.109.026403> for detailed methods.
- [16] S. Heathman, T. Le Bihan, S. Darracq, C. Abraham, D. Deridder, U. Benedict, K. Mattenberger, and O. Vogt, *J. Alloys Compd.* **230**, 89 (1995).
- [17] H.G. Zimmer, K. Takemura, K. Syassen, and K. Fischer, *Phys. Rev. B* **29**, 2350 (1984).
- [18] N.M. Souza-Neto, D. Haskel, Y.-C. Tseng, and G. Lapertot, *Phys. Rev. Lett.* **102**, 057206 (2009).
- [19] Using the lattice parameters determined by x-ray diffraction, we used first principles methods [18,20] to simulate XANES spectra as a function of pressure for both  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  configurations. These reference theoretical spectra were combined to match the experimental data and retrieve the ratio of  $2 + /3+$  valence states. This method takes into account the different shape of XANES spectra corresponding to the two valences, which is ignored in the method of fitting the experimental data with Gaussian peaks [21].
- [20] Y. Joly, *Phys. Rev. B* **63**, 125120 (2001).
- [21] J. Rohler, in *EXAFS and Near Edge Structure III: Proceedings of an International Conference* (Springer, Berlin, 1984), p. 385.
- [22] V. Eyert and W. Nolting, *Solid State Commun.* **60**, 905 (1986).
- [23] E. Alp, W. Sturhahn, and T. Toellner, *Nucl. Instrum. Methods Phys. Res., Sect. B* **97**, 526 (1995).
- [24] U. Klein, G. Wortmann, and G. Kalvius, *Solid State Commun.* **18**, 291 (1976).
- [25] M. M. Abd-Elmeguid and R. D. Taylor, *Phys. Rev. B* **42**, 1048 (1990).
- [26] 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.
- [27] D. Haskel, E. A. Stern, and H. Shechter, *Phys. Rev. B* **57**, 8034 (1998).
- [28] M. Arnold and J. Kroha, *Phys. Rev. Lett.* **100**, 046404 (2008).
- [29] D. DiMarzio, M. Croft, N. Sakai, and M. W. Shafer, *Phys. Rev. B* **35**, 8891 (1987).