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Abstract

Using synchrotron-based Mössbauer and x-ray emission spectroscopies, we explore the evolution of magnetism in elemental (divalent) europium as it gives way to superconductivity at extreme pressures. Magnetic order in Eu is observed to collapse just above 80 GPa as superconductivity emerges, even though Eu cations retain their strong local $4f^7$ magnetic moments up to 119 GPa with no evidence for an increase in valence. We speculate that superconductivity in Eu may be unconventional and have its origin in magnetic fluctuations, as has been suggested for high-T_c cuprates, heavy fermions and iron-pnictides.

I. INTRODUCTION

The discovery of superconductivity in high-T_c cuprates, heavy fermions and, more recently, iron pnictides challenges many of the concepts introduced by the Bardeen-Cooper-Schrieffer theory [1]. Central to this paradigm is the close proximity between magnetically ordered and superconducting phases in these materials and the role that magnetic fluctuations may play in their unconventional pairing mechanism(s) [2-5]. Among the main challenges encountered is their chemical complexity, as the often required charge doping adds an intrinsic inhomogeneity to these systems which leads to the presence of multiple bands near the Fermi level [6, 7]. It would be desirable to investigate a system in which magnetic fluctuations and superconductivity reside in a much simpler host such as an elemental metal.

For many years the rich magnetic properties of lanthanide metals have attracted a great deal of interest [8]. Because of their strong $4f$ local magnetic moments, they are normally not superconducting. Only Ce [9, 10] and Eu [11] are known to become superconducting under pressure. At ambient pressure both Eu and Ce possess local magnetic moments. With increasing pressure Ce undergoes an isostructural γ-α transition near 0.7 GPa with a 16% volume collapse and a strong suppression of Ce's

paramagnetism from Curie-Weiss type to enhanced Pauli paramagnetism [12, 13]. In the α-phase Ce is superconducting with a maximum T_c of 1.7 K at 5 GPa [9, 10]; however, the strongly localized character of the 4*f*-electron state was shown to remain intact [14]. In a few lanthanide- and actinide-based heavy fermion systems, magnetic order coexists with superconductivity, examples being $CePt_3Si$ [15], $CePd_2Si_2$ [3], UPt_3 [16] and URhGe [17]. Superconductivity in proximity to *f*-electron magnetism suggests that magnetic fluctuations may play a critical role in the superconductivity [3, 4]. What is the case for Eu?

As mid-members of the lanthanide series, Eu and Gd both possess seven 4*f* electrons, yielding a sizeable local magnetic moment (J = 7/2). At ambient pressure Eu orders antiferromagnetically at T_N = 90 K [18-21] accompanied by a tetragonal deformation of the bcc lattice [22]. All lanthanide metals except Eu and Yb are trivalent at ambient pressure. It has long been believed that sufficient pressure would drive Eu to a trivalent $4f^6$ state with only weak Van Vleck paramagnetism where superconductivity might appear, as in Am ($5f^6$) [23]. Indeed, Eu was found to be superconducting above 80 GPa with a critical temperature $T_c \approx 2$ K [11]. However, both T_c and its small positive pressure derivative dT_c/dP to 142 GPa lie well below the values found in the nonmagnetic trivalent *spd*-electron metals Sc, Y, La, and Lu [24]. Possible explanations include that the persistence of magnetic order in Eu suppresses T_c or that Eu does not become fully trivalent to 142 GPa. Early x-ray absorption studies on Eu reported a strong increase in valence with pressure, reaching 2.5 at 10 GPa and saturating at 2.64 to 34 GPa [25]. However, recent x-ray absorption experiments, aided by density functional theory under consideration of changes in crystal structure, have shown that Eu remains nearly divalent to at least 87 GPa [26].

To understand the interplay between magnetism and superconductivity in Eu, studies of magnetic properties above 80 GPa are clearly needed. Earlier temperature-dependent electrical resistivity *R(T)* measurements on Eu were limited to 42 GPa [27]. They indicated that the Néel temperature, identified by a kink or bend in *R(T),* decreases slowly with pressure reaching ~80 K at 15 GPa. Above this pressure an additional bend in *R(T)* appears near 140 K, remaining at this temperature to 42 GPa. Two separate Mössbauer spectroscopy studies on Eu were limited to 14 GPa [28] and 27.7 GPa [26], the latter finding no magnetic order above 115 K at 18.6 GPa. An investigation of Eu's magnetism using x-ray magnetic circular dichroism (XMCD) reveals that magnetic order persists to at least 50 GPa with ferromagnetic-like behavior between 20 and 49 GPa [26].

In the present study synchrotron Mössbauer spectroscopy (SMS) and x-ray emission spectroscopy (XES) are combined with megabar diamond anvil cell technology to investigate the evolution of magnetic order and local moment in Eu to pressures exceeding those required to induce superconductivity. The appearance of superconductivity is found to correlate with the disappearance of magnetic order, the strong local moment character persisting to significantly higher pressures.

II. EXPERIMENTAL TECHNIQUES

Synchrotron Mössbauer spectroscopy (SMS) experiments were performed at the 3-ID beamline of the Advanced Photon Source (APS), Argonne National Laboratory. The SMS experiment was carried out at 11 K to pressures as high as 101 GPa using a membrane-driven diamond anvil cell (DAC) and a He flow cryostat [29]. A pair of beveled diamond anvils with 150 μm culet diameter were used to achieve high pressure. Re gaskets were preindented to 25-30 μm thickness and a 65 μm diameter hole was EDM-drilled. The high purity Eu sample (99.98% metal basis) is from the Materials Preparation Center of the Ames Laboratory [30], and from the same sample batch used in superconductivity studies in Ref. [11]. Due to its high reactivity, the sample was loaded into the diamond anvils cells in an Ar filled glove box together with 2-3 ruby spheres. An initial pressure was applied to seal the sample in the glovebox. Subsequent pressures were applied at 11 K. The ruby spheres allow *in situ* pressure determination at 11 K from the R_1 ruby fluorescence line [31]. The synchrotron x-rays were focused to ~30 μm using a pair of Kirkpatrick-Baez mirrors. An avalanche detector with time resolution of 1 ns was used for data collection in the forward direction.

The magnetism in Eu under pressure is probed by the M1 nuclear transition 7/2 → 5/2 in ^{151}Eu at the resonant energy of 21.54 keV [32, 33]. The significant natural abundance 47.8% of the ^{151}Eu isotope makes it unnecessary to artificially enrich the sample. The experiment was performed using the 24-bunches timing mode of the APS with 153 ns separation between the electron bunches. The relatively short half-life of the M1 transition (9.5 ns) makes it possible to extract hyperfine parameters accurately within this time window.

The nonresonant Eu $L_{\gamma 1}$ x-ray XES experiment was performed at beamline 16ID-D of the High Pressure Collaborative Access Team (HPCAT) of the APS. Pressures up to 119 GPa were generated using a symmetric cell with two opposing anvils beveled to 150 μm culet diameter. A Be gasket was used due to its low x-ray absorption. To achieve Mbar pressures, the Be gasket was first pre-indented to 40 μm and then about 80% of the culet area was drilled out and filled with c-BN/epoxy. The gasket was then further pre-indented to about 25 μm and a 60 μm hole was laser drilled at the center of the c-BN insert as a sample chamber. Ruby spheres and an Eu sample from the same batch used in the SMS experiment were loaded into the DAC. Pressures above 60 GPa were determined using the diamond anvil Raman gauge [34].

The 8 keV x-ray beam was focused down to ~30 μm (V) × 50 (H) μm with Kirkpatrick-Baez mirrors. Incident and emitted x-rays went through the Be gasket, emission collected at 90º from the incoming beam. XES spectra were collected at room temperature using an AmpTek solid state detector coupled to a Si (620) analyzer. The data were normalized to the incident beam intensity.

III. RESULTS AND DISCUSSION

The present SMS studies on Eu were carried out in five experimental runs up to 101 GPa. Representative SMS spectra of Eu under pressure at 11 K are shown in Fig. 1. The experimental data are fitted by adopting the dynamical theory of nuclear resonant

scattering as implemented in the CONUSS program [35]. The analysis of SMS spectra was performed by fitting the data with two hyperfine parameters (hyperfine magnetic field and quadrupole splitting) and thickness, which is related to the sample effective thickness. Fitting to a distribution of magnetic field was also attempted but it turned out to be negligible. To compare with earlier Mössbauer studies [28], the energy-domain spectra are simulated in CONUSS using the parameters obtained by fitting the time-domain data, as shown in the right column of Fig. 1. Since the isomer shift at 11 K is not determined in this experiment, the values of the isomer shift are placed at zero in the simulations. In the absence of hyperfine splitting of nuclear levels, the SMS spectrum displays a logarithmic decay of nuclear forward scattering intensity corresponding to a singlet spectrum in conventional Mössbauer spectroscopy. In the presence of magnetic order, oscillations emerge in the time-domain SMS spectrum due to Zeeman splitting of nuclear levels. Quadrupolar splitting (QS) in non-cubic environments adds an additional frequency component. SMS spectra at 8 and 12.3 GPa agree well with those reported in previous studies [28]. An increase in the oscillation frequency as the pressure increases implies increasing hyperfine magnetic field strength.

The oscillations are seen to disappear twice, in a narrow pressure range around 42 GPa (Fig. 2) and above 80 GPa (Fig. 1). Around 42 GPa, quantum beats in the SMS spectra disappear (Fig. 2); this was observed at 41 GPa in experiment run 5 and 44 GPa in run 3, indicating that the magnetic hyperfine field becomes negligible in this narrow pressure range. High resolution x-ray diffraction studies [36] show Eu undergoes a first order phase transition from one monoclinic incommensurate phase to another incommensurate phase around 38 GPa. Between 38 GPa and 42 GPa Eu is in a mixed phase. For the spectrum collected at 44 GPa (run 3) a fit to the data with zero magnetic hyperfine field is shown in red, which is consistent with the presence of a single phase observed above 42 GPa in diffraction studies [36]. At 41 GPa the spectrum clearly shows the hyperfine field to be rather small.

The extracted hyperfine parameters at 11 K, the magnitude of the hyperfine field $|H_{hf}|$ and QS, are plotted in Figs. 3(a) and 3(b), respectively, as a function of applied pressure. The sign of H_{hf} was not determined in this experiment (zero external field), but is known to be negative at ambient pressure [28]. The extrapolation of hyperfine field from the present data to ambient pressure gives $|H_{\mathrm{hf}}| = 26.5$ T, consistent with the reported value at 4.2 K [20].

Magnetic order in Eu is driven by indirect RKKY-interactions between localized $4f^7$ moments mediated by conduction electrons. The magnetic hyperfine field H_{hf} is a sum of three contributions

$$H_{\mathrm{hf}} = H_{\mathrm{C}} + H_{\mathrm{CE}} + H_{\mathrm{n}},$$

where H_{C} represents the core electron polarization contribution with a value at ambient pressure of -34 T, H_{CE} is due to polarization of conduction electrons by Eu's own 4*f* electrons contributing +19 T, and the third term, H_{n} = -11.5 T, originates from polarization of conduction electrons by neighboring atoms [37-40]. The sum of these three terms results in the net negative hyperfine field of -26.5 T at ambient pressure [20].

H_C is considered to be weakly dependent on pressure [39], thus the pressure

dependence of the hyperfine field is likely due to changes in H_{CE} and H_n. The initial decrease with pressure up to 12 GPa in $|H_{hf}|$ seen in Fig. 3(a) has been interpreted by others [28, 40] as arising mainly from an increase in the *positive* contribution, H_{CE}, as the conduction electrons are compressed to a smaller volume. The abrupt increase in $|H_{hf}|$ at 12 GPa is likely due to the well known bcc-to-hcp phase transition [41- 43]. We speculate that there may be a sign change to positive in H_n, and, therefore, in H_{hf}, as would occur in a transition from antiferromagnetic to ferromagnetic order. This scenario is supported by the result of an earlier XMCD experiment where ferromagnetic behavior in Eu was observed to emerge near 20 GPa [26]. The downward spike in $|H_{hf}|$ near 40 GPa is likely the result of a sign change of H_{hf} at the first order Eu-IV to Eu-V structural transition [36,44]. A clear understanding of the effects of pressure-induced structural phase transitions requires determining changes in both the sign and magnitude of H_{hf}.

Above 81 GPa the hyperfine field is seen to fall rapidly to zero, indicating that Eu no longer orders magnetically above 11 K. At 91 GPa the magnetic order is completely suppressed. The critical pressure at which Eu loses magnetic order is estimated to be 84 GPa, extrapolated from the data at 81 GPa and 82.5 GPa. It is significant that this pressure is the same as that (84 GPa) where superconductivity in Eu first appears at 1.8 K in magnetic susceptibility measurements; in the same study no superconductivity was observed above 1.4 K at 76 GPa [11]. While it is evident that pressure suppresses magnetism and induces superconductivity in Eu near 80 GPa, the precise phase boundaries remain to be accurately determined. It is noteworthy that in the pressure region 70 - 92 GPa *no structural phase transition* in Eu was observed [42].

The QS has lattice and electronic contributions; the latter originates in the aspherical electron density of a partially filled inner shell (the 4*f* shell in the case of Eu) [45, 46]. In the case of divalent Eu ions, the 4*f* shell is half filled ($4f^7$); based on Hund's rule, the electronic ground state is the isotropic $^8S_{7/2}$ state, which gives no electronic contribution to QS [47]. For trivalent Eu ions, the $4f^6$ orbital results in a $^7F_0$ configuration with no net angular momentum [46]. Therefore, in either case the QS arises solely from the lattice contribution. QS is zero below 12 GPa in the bcc phase, but it increases monotonically from 12 to about 30 GPa (Fig. 3(b)) due to the lower symmetry of the hcp phase. The structure in QS at higher pressures is likely related to the known sequence of structural transitions. To fully interpret the quadrupole splitting data, further high-resolution x-ray diffraction experiments at pressures above 50 GPa, preferably at low temperature, are needed. It is worth pointing out that extracted quadrupole splitting values of a few mm/s are typical for Eu ions, for example 8.3 mm/s in $EuCl_2$ and 11.5 mm/s in $EuSO_4$ [48]. An exception is $EuRh_3B_2$ where the anomalously high value of 48 mm/s was observed, a result of the extremely short Eu-Eu separation [49, 50].

Superconductivity in Eu above 80 GPa appears to be correlated with the collapse of magnetic order seen in the present SMS study. However, the nature of Eu's 4*f* moment in the nonmagnetic/superconducting state is still unknown. To shed some light on this question we performed a $4d \rightarrow 2p$ $L_{\gamma 1}$ XES experiment under pressure to 119 GPa (Fig. 4). The intra-atomic exchange interaction between the 4*f* and 4*d* core levels in the final state of the emission process leads to a satellite peak at lower energy. The intensity ratio of the

satellite to the main band in the $L_{\gamma 1}$ line reflects the size of the atomic 4*f* moment [14, 51-53]. In Ce the satellite intensity of the $L_{\gamma 1}$ emission line decreases significantly across the γ-α volume collapse and was interpreted as the result of a significant increase in *f-d* hybridization [14]. However, in the case of Eu, no change in the $L_{\gamma 1}$ line of Eu is observed up to 119 GPa (Fig. 4). This indicates that the highly localized character of the $4f^7$ magnetic state in Eu remains intact without a measurable increase in *f-d* hybridization, as found in earlier XES studies on Gd [54] and Tb [53]. This validates recent x-ray absorption experiments showing that Eu remains nearly divalent to at least 87 GPa [26] and extends these findings beyond the pressure regime where superconductivity first emerges at low temperature. The persistence of local moments across magnetic-superconducting phase transitions has been observed in superconductors with possible unconventional pairing, including Ce [14] as well as $CeCu_2Si_2$, $YbRh_2Si_2$, $CeRhIn_5$, and most recently CeNiAsO [55-61]. In these systems, as in Eu above 80 GPa, the proximity of the superconducting state to a magnetically ordered phase raises the possibility that spin fluctuations may be important in the pairing interaction. Unfortunately, the present experiments are not able to clearly identify the physical mechanism(s) responsible for the demise of magnetic order and the emergence of superconductivity in Eu above 80 GPa.

Whether or not this transition can be described as a quantum phase transition with a quantum critical point (QCP) is beyond the scope of the present experiments. Admittedly, a magnetic QCP in Eu near 80 GPa would be reminiscent of the behavior of some heavy fermion systems and Fe-pnictides under the action of magnetic field, external pressure or chemical pressure [3, 15-17, 62]. In some heavy-fermion systems superconductivity appears to emerge near a QCP from within a Kondo lattice state [63, 64]. Although a Kondo lattice model may account for the pressure-induced loss of magnetic order and emergence of superconductivity in trivalent Ce [14], an element sporting only a single 4*f* electron, the full screening of *seven* 4*f* electrons on each Eu ion by two conduction electrons (per Eu atom) would seem highly unlikely. A full exploration of the pressure-induced changes in this chemically simple but physically complex metal may provide a pathway to understanding the role of magnetic fluctuations in other unconventional superconductors.

In summary, we have investigated the effect of pressure on magnetic order and the highly localized magnetic moment of Eu to pressures exceeding 1 Mbar using SMS and XES synchrotron spectroscopies. The magnitude of the magnetic hyperfine field increases to more than twice its ambient pressure value at intermediate pressures, but collapses above 80 GPa where superconductivity emerges. The proximity to a magnetically ordered phase, together with the persistence of strong local moments in the superconducting phase, points to the possibility that magnetic fluctuations may be involved in the superconducting pairing mechanism of this interesting rare-earth metal.

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FIGURE CAPTIONS

Figure 1. (left column) Representative SMS spectra of Eu at high pressure and 11 K. Black dots are data and red lines are fits from CONUSS. (right column) Simulated spectra in energy domain from fits of the time-domain data (red lines in left column).

Figure 2. SMS spectra at 41 GPa from run 5 and 44 GPa from run 3. The very weak oscillations indicate negligible hyperfine field $|H_{hf}|$ at these pressures.

Figure 3. Extracted hyperfine parameters from SMS spectra at 11 K. (a) Absolute value of magnetic hyperfine field $|H_{hf}|$ versus pressure compared to previous high pressure studies by Farrell and Taylor at 44 K [27]. Dashed lines through data are guides to the eye. Lower right: superconducting transition temperature T_c versus pressure from Ref. [11]; blue straight line gives slope dT_c/dP = 18 mK/GPa. (b) Quadrupole splitting (QS) versus pressure. Error bars come from CONUSS fits to $|H_{hf}|$ and quadrupole splitting.

Figure 4. $L_{\gamma 1}$ XES spectra of Eu to pressures of 119 GPa at room temperature, normalized to main peak intensity. Vertical lines show peak positions for main band and satellite peak. No apparent change in XES spectra was observed under pressure, suggesting no change in 4*f* magnetic moment to 119 GPa.

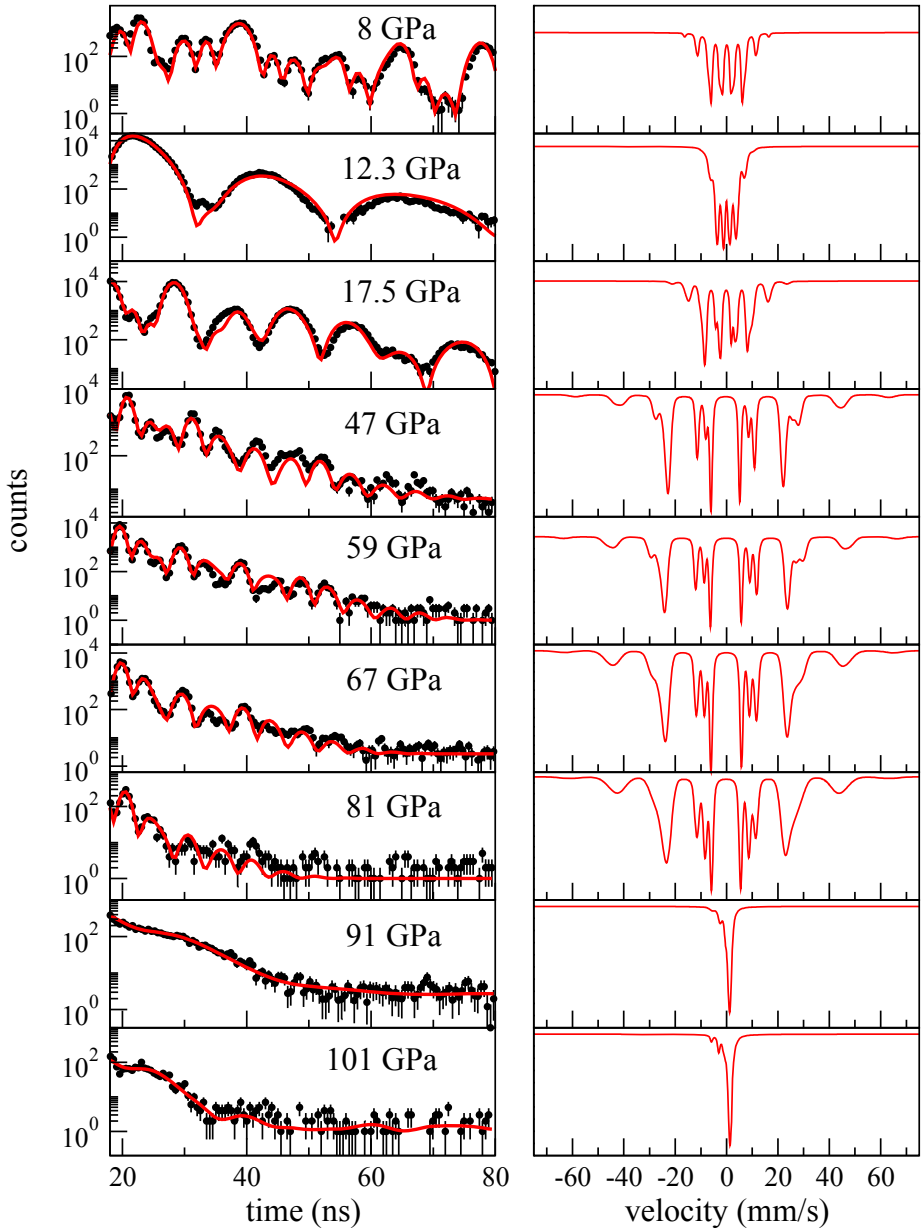
8 GPa
12.3 GPa
17.5 GPa
47 GPa
59 GPa
67 GPa
81 GPa
91 GPa
101 GPa
counts
time (ns)
velocity (mm/s)

Figure 1.

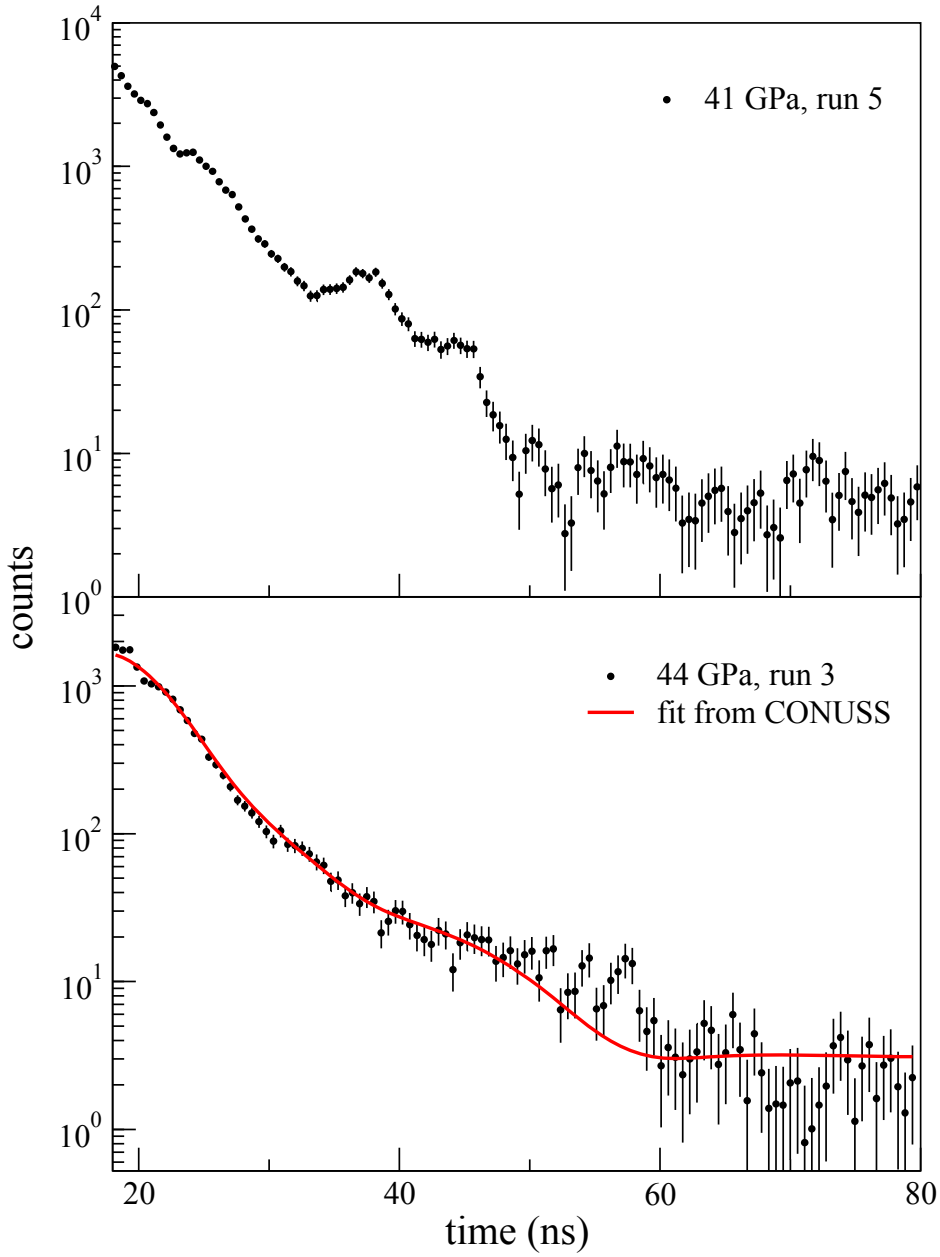
counts
time (ns)
41 GPa, run 5
44 GPa, run 3
fit from CONUSS
10^0
10^1
10^2
10^3
10^4
20
40
60
80

Figure 2.

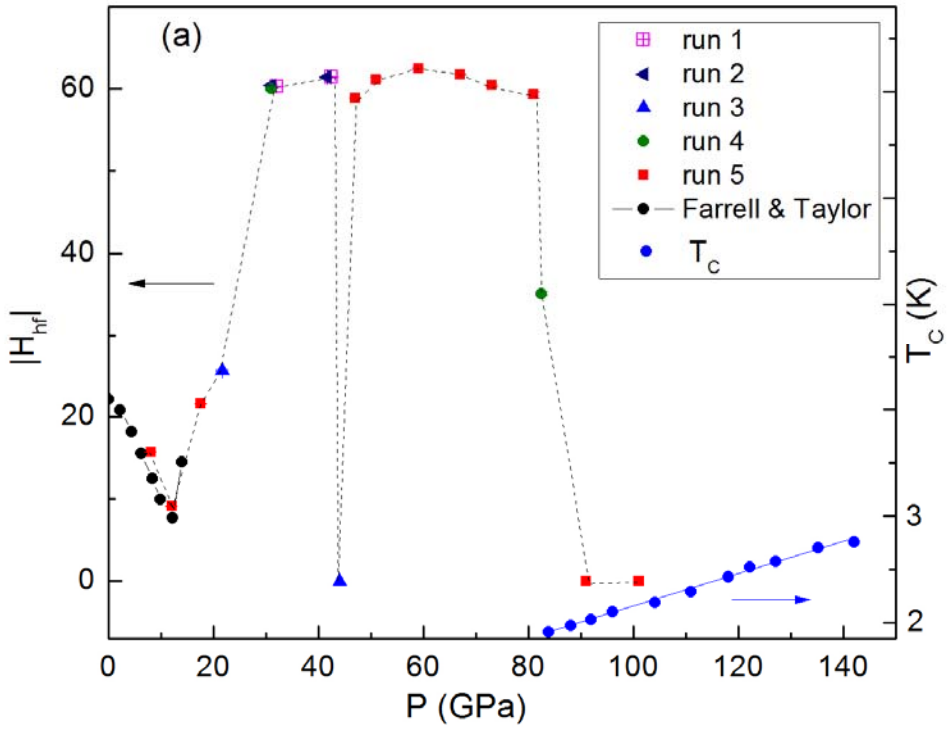
(a)
run 1
run 2
run 3
run 4
run 5
Farrell & Taylor
T_c
$|H_{hf}|$
T_c (K)
P (GPa)
0
20
40
60
80
100
120
140
2
3

Figure 3(a).

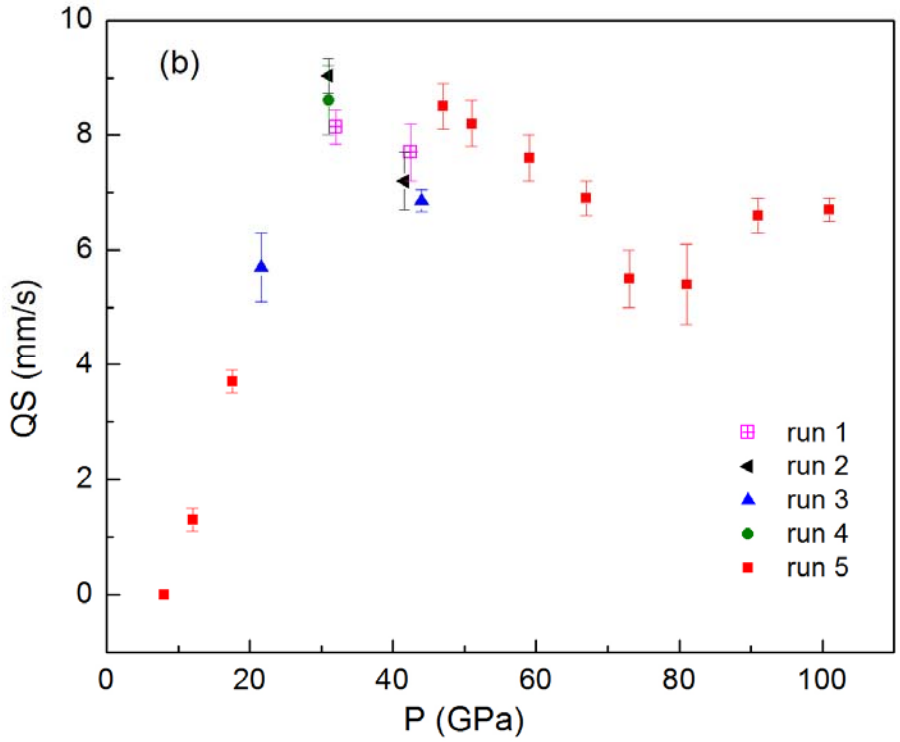

Figure 3(b).

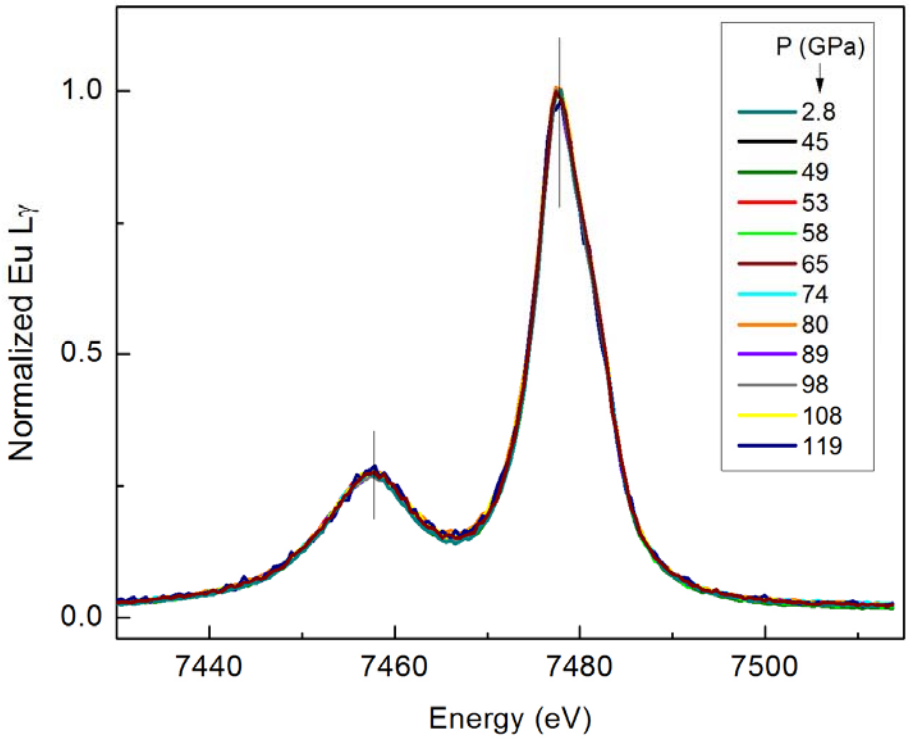
P (GPa)
2.8
45
49
53
58
65
74
80
89
98
108
119
Normalized Eu Lγ
1.0
0.5
0.0
7440
7460
7480
7500
Energy (eV)

Figure 4.