ESRF	**Experiment title:** Phonon density of states in Eu metal under high pressure measured by ^{151}Eu nuclear inelastic scattering	**Experiment number**: HS-3289
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Names and affiliations of applicants (* indicates experimentalists):

Gerhard Wortmann*, Ulrich Ponkratz*, Bernd Bielemeier* (Universität Paderborn, Department Physik, 33095 Paderborn, Germany

Kirsten Rupprecht* (Tierärztliche Hochschule Hannover, 30173 Hannover, Germany)

Report:

Eu metal and Yb metal are divalent due to their position in the series of 4f elements, while all other rare-earth metals are trivalent. Their molar volumes are 45% (Eu) and 38% (Yb) larger than that of the neighbouring trivalent metals. Their structures, bcc for Eu and fcc for Yb, resemble those of divalent alkali-earth metals [1]. Under pressure, both metals become mixed-valent (m.v.), that means the $4f^7$ and $4f^{14}$ configurations change towards the trivalent $4f^6$ and $4f^{13}$ configurations. These valence changes can be monitored by Mössbauer and RE L_3-edge spectroscopy [2, 3, 4]. Both Eu and Yb, even when transformed into the hcp structure as the other RE^{3+} metals, do not exhibit a full valence transition, the valence v do not exceed the so-called thermo-dynamic limit, that is v = 2.65 for Eu and v = 2.89 for Yb [4]. The elastic properties of Eu metal in the m.v. state is of actual interest, e.g. in comparison with the actinide metals with delocalized 5f-(band)electrons [5]. In the m.v. bcc-phase above 5 GPa, Eu metal exhibit an unusual large compressibility despite the fact that the molar volume is already smaller than that of Gd, the neighbouring trivalent metal [1].

In this beamtime we performed at RT ^{151}Eu nuclear inelastic scattering (NIS) studies of Eu metal in the bcc phase at 10 GPa and in the hcp phase at 17 GPa, well above the bcc-hcp transition at 12.5 GPa. In addition we performed ^{151}Eu nuclear forward scattering (NFS) studies to check the quality of the pressurised Eu sample against Eu^{3+} impurities as well as for determining the isomer shift with respect to an EuS reference absorber, allowing a direct determination of the Eu valence and comparison with a previous ^{151}Eu-Mössbauer study of Eu metal up to 14 GPa [2]. In addition, we performed a ^{151}Eu-NIS study of an Eu metal absorber placed in a cryostat at 100 K in order to extract the phonon-DOS at ambient pressure. Due the low Debye temperature (Θ_D = 94 K) of Eu metal and the corresponding low Mössbauer-Lamb factor, f_{LM} = 0.03 at RT, ^{151}Eu-NIS spectra taken at RT are dominated by multi-phonon excitations, making an extraction of the phonon-DOS impossible, as shown in ^{119}Sn-NIS studies of tin metal (ß-Sn) [6]. Even at 100 K, the extraction of the phonon-DOS was hampered by multi-phonon excitations. Evaluation is still in progress, using a new analytical approach, which was just approved for a recent ^{149}Sm-NIS study of SmS at high pressure [7].

The high-pressure studies were performed with a diamond anvil cell specially designed for NIS studies. Pure Eu metal was loaded under inert conditions into a 300 µm hole of a Beryllium gasket without a pressure transmitting medium. A high-resolution monochromator provided a bandwidth of 1.3 meV. For the ^{151}Eu-NIS studies an energy range of +/- 40 meV was scanned with a step width of 0.25 meV around the ^{151}Eu resonance (21.542 keV). Typically about 40 spectra, each collected in approximately 30 minutes, were measured and summed up afterwards. As mentioned above, sample purity was proven by ^{151}Eu-NFS spectra. The NFS signals exhibited a pure exponential decay; indicating the absence of Eu^{3+} contamination (like Eu_2O_3), which would has caused a quantum beating against the Eu sample. In the ^{151}Eu-NFS spectra with an additional EuS reference absorber the quantum beating was used to determine the isomer shift of the

pressurised Eu metal (Fig. 1). The evaluated isomer shifts (IS) agree with those of the previous Mössbauer study [2], the small and systematic differences of the IS values in Fig.1 are due to different temperatures in these studies. The derived valences of v = 2.35(5) for 10 GPa and of v = 2.50(5) for 17 GPa agree well with those derived at RT in [3].

Fig. 2 shows the ^{151}Eu-NIS spectra of Eu metal at 10 GPa (bcc phase) and 17 GPa (hcp phase). The evaluation of the phonon-DOS from the spectra of the bcc phase was hampered by a low statistical accuracy and multi-phonon excitations, so the derived phonon-DOS should be considered as preliminary. It should be mentioned that the increase in the Debye temperature and f-factor, respectively , did not correspond to the expectation of the Debye model for a reduction of the molar volume by ~40% at 10 GPa, pointing again to the anomalous high compressibility in the strongly m.v. bcc-phase [1]. The evaluation of the phonon-DOS for the hcp phase at 17 GPa with a reduction of the molar volume by ~50% [1] is much more reliable and is well comparable with the phonon-DOS of other RE^{3+} metals, e.g. Ho and Tb [8] as it exhibits a three peaked structure with a well-resolved maximum for the optical phonons, characteristic for the hcp structure, at ~12 meV. A preliminary evaluation of the DOS yields slightly smaller values for the Debye temperature than reported for Ho and Tb.

References: 1. K. Takemura and K. Syassen, J. Phys. F: Metal Phys.15, 543 (1985). **2.** J.N. Farrell, R.D. Taylor, PRL 58, 2478 (1987). **3**. K. Syassen, G. Wortmann, et al., PRB 26, 4745 (1982); A. Fuse et al., J. Alloys Comp. 376, 34 (2004). **4**. J. Röhler, in: Handbook on the Physics and Chemistry of the Rare Earths (North Holland, 1987), Vol. 10, chap. 71, p. 453 and references therein. **5**. S. Heathman et al., Science 309, 110 (2005); ESRF Highlights 2005, p.31. **6**. A. Barla et al., Phys. Rev. B 61, R14881 (2000). **7**. U. Ponkratz, A. Barla, J.P. Sanchez, R. Rüffer, G. Wortmann, preprint. **8**. Landolt-Börnstein, New Series Vol. 13 (Springer, Berlin 1981), p. 64 (Ho) and 144 (Tb).

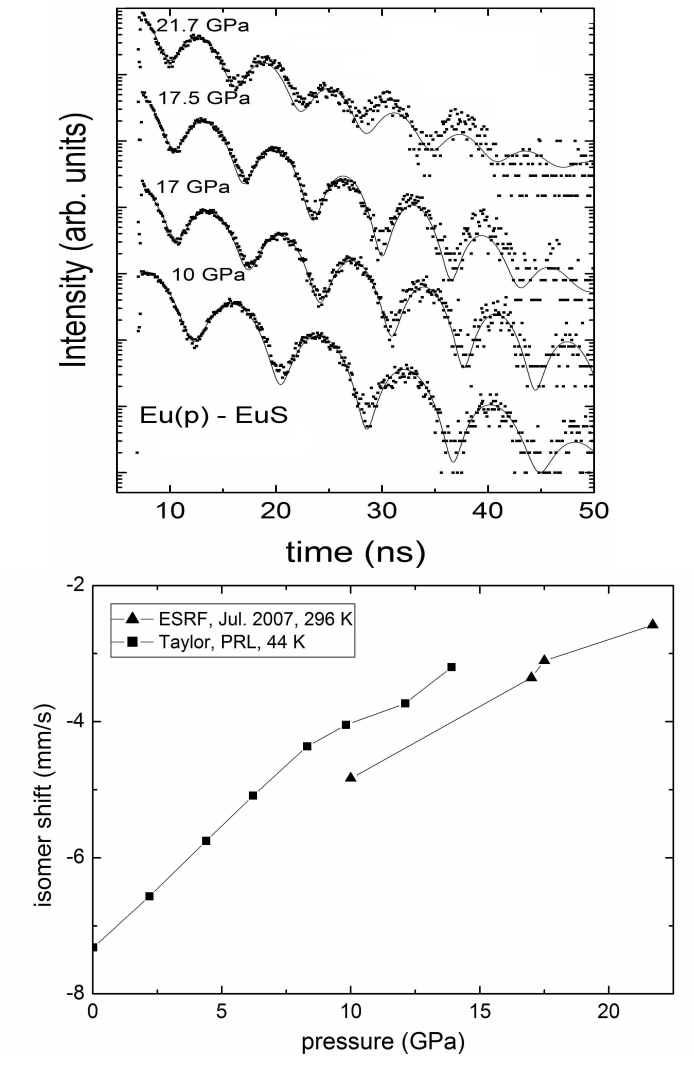

Fig. 1 (above) ^{151}Eu-NFS spectra of Eu metal at various pressures vs. EuS. (below) Comparison of derived isomer shifts with Ref. 2 (measured at lower temperature).

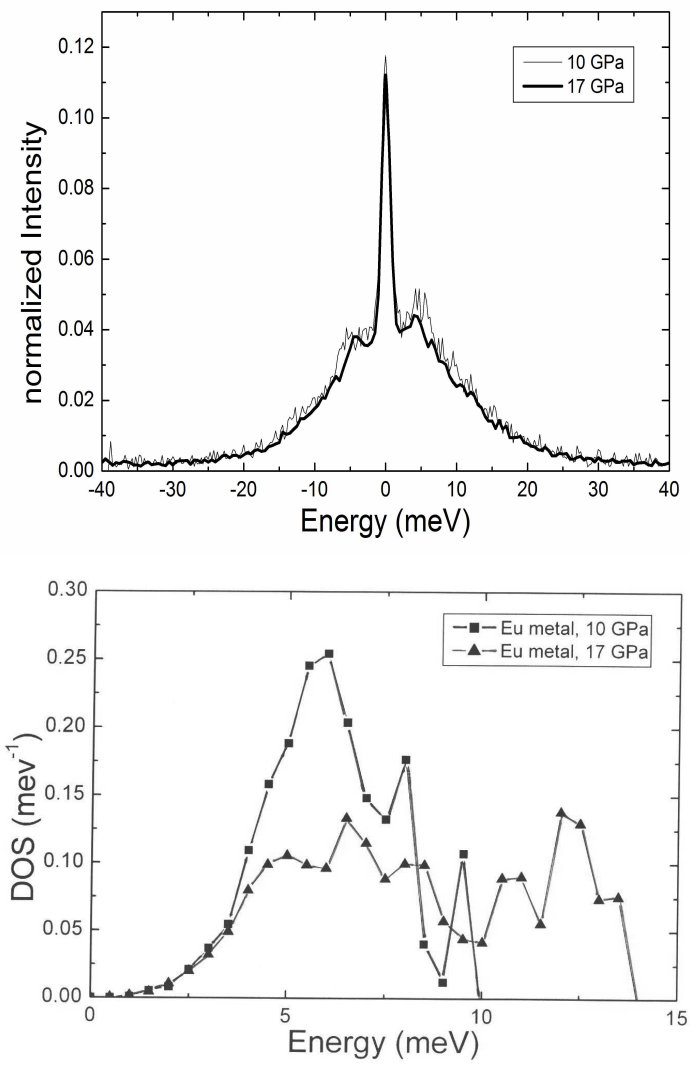

Fig. 2 (above): ^{151}Eu-NIS spectra of Eu metal in the bcc phase at 10 GPa and in the hcp phase at 17 GPa. (below) Derived phonon-DOS from the above NIS-spectra.