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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **Eu magnetism at extreme conditions: Magnetism in EuO and EuS at pressures up to 1 Mbar**	**Experiment number:** HE-1690
Beamline: ID22N	**Date of experiment:** from: 11.05.04 to: 17.05.04	**Date of report:** 31.08.04
Shifts: 18	**Local contact(s):** **Dr. Rudolf Rueffer**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report: The present experiments were based on our successful proposals HE-592 and HE-1490, where we performed nuclear-forward scattering (NFS) experiments with the 21.5 keV Mössbauer radiation of Eu-151 and studied for the first time the magnetic properties of the Eu(II)-chalcogenides EuS, EuSe and EuTe in their CsCl-type high-pressure phases [1, 2].

The present proposal had the ambitious goal to reach the 1 Mbar (= 100 GPa) range for these studies. We reached this goal and studied EuS up to 120 GPa, by far the highest pressure where, to the best of our knowledge, the electric and magnetic properties of a Eu-system (or even a rare-earth system) has been studied. We did not study, as proposed, EuO, since the quality of our sample was not good enough (Eu^{3+} impurities, as proved by ^{151}Eu-Mössbauer spectroscopy). Therefore we switched to EuSe, which we had investigated in the CsCl-phase already up to 48 GPa (see HE-1490 report). For both EuS and EuSe we could increase the Curie temperature up to 295 K for EuS at 120 GPa and 300 K for EuSe and observe a strongly magnetic and mixed-valent state of the Eu ions, a new observation for the Eu-chalcogenides.

Like in the experiment HE-1490 we used advanced focusing optics to concentrate the whole monochromatized synchrotron radiation on the small samples (0.10 to 0.15 mm diameter) contained in a miniature diamond anvil cell (DAC). The DAC was mounted in a He cryostat equipped with a superconducting magnet. By use of these external fields we had determined the ordering type in EuS, EuSe and EuTe in the their CsCl-phases as ferromagnetic. In addition we observe at high pressures a strong magnetic texture with the axis of magnetization along the diamond anvil axis, and therewith parallel to the SR, which simplifies the normally complex ^{151}Eu-NFS-spectra to a simple periodic beat structure (see Fig. 1 and Ref. 1). The ^{151}Eu-NFS-spectra were recorded in the following sequence: For each new pressure, we measured first at 300 K NFS spectra with EuF$_3$ and EuS as Eu^{3+} and Eu^{2+} reference absorbers in order to obtain isomer shifts S_{IS} of the pressurized samples [1, 2]. Then we went to low temperature to obtain the saturation value of the magnetic hyperfine field B_{hf} ($T \rightarrow 0$ K). By measuring NFS-spectra at increasingly higher temperatures, the magnetic ordering temperature T_C was determined (Fig. 1).

Fig. 2(a) shows the derived values of T_C for EuS and EuSe together with our previous data as a function of the Eu-Eu distance. The structural information (p-V relationship) was determined by us from EDX measurements performed at the beamline F3 at HASYLAB [3]. Fig. 2(b) shows the measured isomer shifts S_{IS} and the derived valences states v´ for EuS and EuSe. For details to these derived information on the valence state v´, which is also reflected by values of the hyperfine fields B_{hf}, not shown here, we refer to Ref. 4.

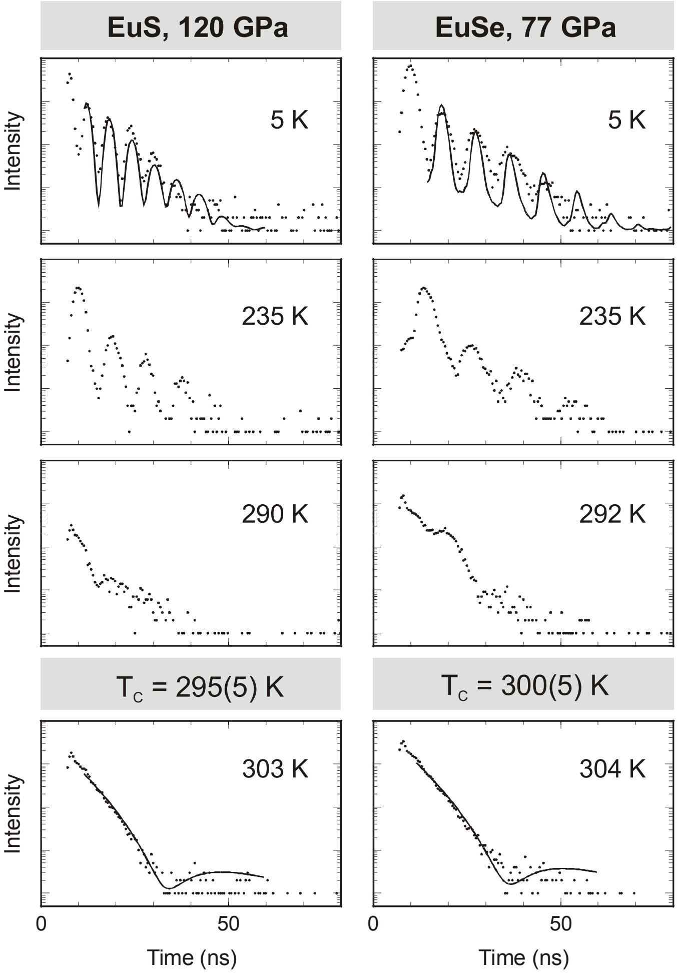

Fig. 1: Selected ^{151}Eu-NFS spectra of EuS and EuSe at the highest pressures. At low temperature, they exhibit periodic beat pattern, indicating strong magnetic texture. At highest temperatures, the (flat) NFS-spectra exhibit only a Bessel minimum from absorber thickness effects, but no magnetic inter-actions.

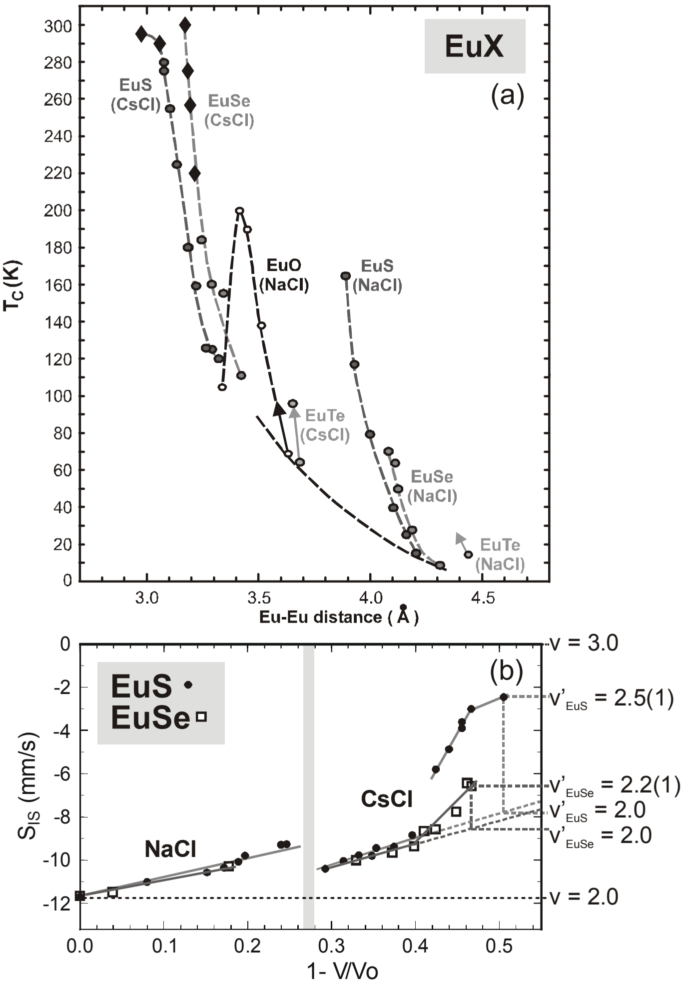

Fig. 2: (a) Curie temperature T_C for EuX (X = O, S, Se, Te) as function of the Eu-Eu distance. The new results are the full diamonds for EuS and EuSe in the CsCl-phases. Data for EuO, EuS and EuSe (NaCl-phases) are from [6, 7]. (b) Isomer shift S_{IS} for EuS and EuSe from the present NFS-data as function of the normalized atomic volume. The dotted lines correspond to the variation of S_{IS} due to the reduced volume, the full line to volume and valence changes with the derived valencies v´.

For EuS, going from 88 GPa to 120 GPa, we observe a small, but continuing increase of T_C to 295 K, accompanied by a relatively small increase of the isomer shift corresponding to value of v´ = 2.5(1) at 120 GPa. This is a surprising behaviour, when one compares with the case of EuO in the NaCl-phase, where with the onset of mixed valence a reduction of the magnetic ordering was observed [5, see also Fig. 2(a)]. The observed behaviour of EuS resembles the case of Eu metal, where at highest pressures a saturation of the Eu valence at 2.64, the thermodynamic limit, was observed [6].

For EuSe, going from 48 GPa to 77 GPa, we observe a steeper increase of T_C as expected and reach T_C = 300 K already at 77 GPa. The corresponding values of S_{IS} and the derived valence of v´ = 2.2(1) clearly indicate a less mixed-valent state than for EuS: From Fig. 2(a) we expect for EuSe, at higher pressures, considerably higher values of T_C than 300 K.

The outstanding success of this beamtime is based on the excellent experimental conditions established now at beamline ID22N together with the longstanding expertise with the ^{151}Eu-resonance at ESRF [1,2,8]. This beamtime coincided for one of us (K.R.) with the finalising of the PhD work, concerned mainly with these ^{151}Eu-NFS studies [4].

References: [1] O. Leupold, K. Rupprecht, G. Wortmann, Structural Chemistry 14, 97-107 (2003). [2] R. Lübbers, K. Rupprecht, G. Wortmann, Hyperfine Interactions 128, 115–135 (2000). [3] K. Rupprecht, U. Ponkratz, G. Wortmann, HASYLAB Report 2003, p.605. [4] K. Rupprecht, PhD thesis, Universität Paderborn (2004). [5] M.M. Abd-Elmeguid, R.D. Taylor, Phys.Rev. B 42, 1048 (1990). [6] J. Röhler, Handbook of the Physics and Chemistry of Rare Earths, Vol. 10, 523 (1987). [7] I.N. Goncharenko and I. Mirebeau, Phys. Rev. Lett. 80, 1082 (1998). [8] O. Leupold et al., Europhys. Lett. 35, 671 (1996).