

Valence fluctuations in ternary europium compounds*

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We outline the possibility to study europium valence fluctuations with the μ SR method and report on μ SR experiments on the intermetallic compounds EuPdAs and NdPdAs. Above a magnetic transition at 15 K the temperature dependence of the relaxation rate in the trivalent neodymium system behaves like a typical localized moment system. In the valence fluctuating europium compound the zero field relaxation rate levels off at $1.0 \mu\text{s}^{-1}$ above 40 K. Furthermore, the relaxation enhancement in transverse field experiments is much smaller than expected for a pure dipolar coupling. Therefore an isotropic hyperfine coupling of typical strength is assumed and a valence fluctuation rate of $0.8 \mu\text{s}^{-1}$ at 200 K is derived. Below the magnetic transition at 5 K a disordered spin freezing is concluded in EuPdAs.

It is well known that some europium intermetallic compounds like EuPtP, EuPdAs and EuNiP (hexagonal Ni_2In structure) and EuCu_2Si_2 , EuNi_2P_2 and EuPd_2Si_2 (tetragonal ThCr_2Si_2 structure) show a peculiar mixed valent behaviour [1,2]. In all these compounds the intermediate valence of Eu is temperature dependent: at room temperature the Eu state is close to Eu^{2+} ($S = J = 7/2$), at low temperatures there is a tendency to Eu^{3+} ($J = 0$, diamagnetic ground state).

In this work we concentrate on EuPdAs in which the mean valence of the europium changes from $+2.15(5)$ at room temperature in a first order transition at ≈ 175 K to a value of $+2.35(5)$ below 100 K. This behaviour has been concluded from lattice constant and dc-susceptibility measurements as well as Mössbauer and L_{III} -edge spectroscopy [3]. From an analysis of the absorption line width the ^{151}Eu Mössbauer experiments reveal a very low valence fluctuation (VF) rate ν_{VF} with an upper limit of 10^8 s^{-1} in the whole temperature range. In a recent comparison of different intermediate valence compounds of the EuTX series a quasistatic triangular or hexagonal arrangement of the Eu^{2+} and Eu^{3+} in the Eu-planes has been concluded [1].

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Below 5 K the susceptibility measurements indicate the onset of antiferromagnetic correlations [3]. These give rise to frustration effects in the triangular intra-plane coordination of the Eu^{2+} spins which we want to study with a local microscopic probe.

Our primary interest is, however, to study the valence fluctuation in these europium compounds via μSR . The very different magnetic moments of Eu^{2+} (free ion value $\mu_{\text{eff}} = 7.94\mu_{\text{B}}$) and Eu^{3+} ($\mu_{\text{eff}} = 0$) lead to a distribution of the magnetic coupling via dipolar and hyperfine interaction at the muon site. In the hexagonal systems the most probable muon site is at or close to the center of Pd/As hexagons between two rare earth layers. In a simple model we consider only dipolar fields at the muon site caused by the two nearest neighbour europium ions along the crystallographic c -axis. For a calculation of the muon frequency spectrum in a transverse field μSR experiment we use the mean paramagnetic polarisation according to a Curie law. An external field along the c -axis then causes a muon Knight shift (KS) of +1.1% at 200 K or +2.2% at 100 K per nearest neighbour Eu^{2+} . From the mean valence the relative probabilities for the muon site to have two, one or none nearest neighbour magnetic ions are calculated to 25:10:1 above and 4:4:1 below the valence transition, respectively. These ratios directly apply to the intensities of the corresponding spectral lines.

So far only a static arrangement of the europium valence has been considered. The effect of a fluctuating valence can be taken into account qualitatively in analogy to other fluctuation phenomena (e.g., as seen in NMR experiments [5]). The fluctuation rate ν_{VF} has to be considered with respect to two important time scales: the experimental line width of a single muon resonance line ν_{exp} and the line separation $\Delta\nu$ due to the different muon surroundings. For an observation of the valence fluctuation, the line separation must be equal, or better, larger than the experimental line width ($\nu_{\text{exp}} \leq \Delta\nu$). The shape of the frequency spectrum is controlled mainly by the ratio of ν_{VF} versus $\Delta\nu$. In the static case ($\nu_{\text{VF}} \ll \Delta\nu$), two lines with their natural line width ν_{exp} occur. These lines are asymmetrically broadened and shifted towards each other in the intermediate regime ($\nu_{\text{VF}} \approx \Delta\nu$). In the motional narrowing limit ($\nu_{\text{VF}} \gg \Delta\nu$), a single line at an intermediate frequency is observed. The natural line width is enhanced to $\nu_{\text{exp}} + \Delta\nu^2/\nu_{\text{VF}}$ in this case.

In the transverse field μSR experiment, the line separation $\Delta\nu$, and therefore, the fluctuation time window can be controlled by the external field strength. Considering a Knight shift difference of the order of 1% between the different muon surroundings, a typical line splitting in 0.1 T transverse field is 1.5 MHz. This results in a relaxation time window 2–3 orders of magnitude below the Mössbauer effect which in valence fluctuation studies is regarded as the microscopic method with the slowest time window.

However, a specific problem in these TF μSR experiments arises if the valence fluctuation frequency is of the order of the inverse muon lifetime. The phase coherence in the muon spin spectrum is destroyed by the uncorrelated changes of the individual muon surroundings which might lead to a significant loss of signal amplitude. In this case the use of the muon spin resonance technique (RF- μSR) may be necessary to recover the full line intensities.

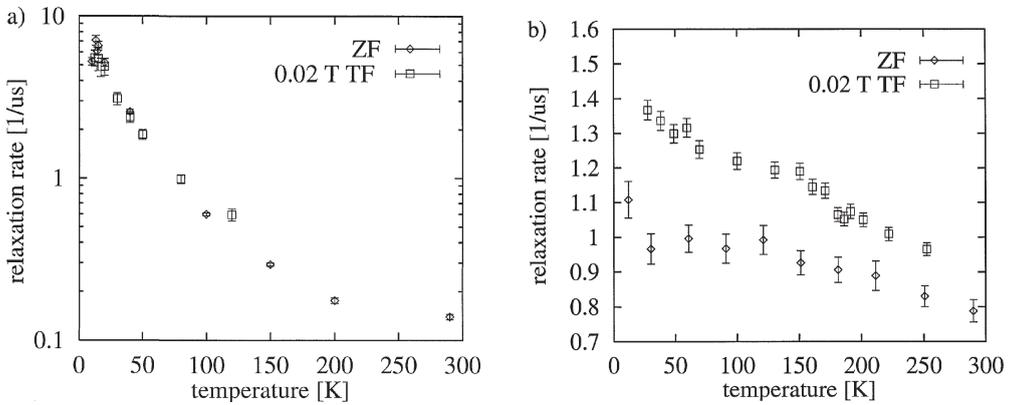


Fig. 1. Zero field (ZF) and transverse field (TF) relaxation rates in (a) NdPdAs and (b) EuPdAs.

We have studied a powder sample of EuPdAs in zero field (ZF), longitudinal field (LF) and low transverse field μ SR experiments in the MUSR beamline at the ISIS pulsed muon source between 2 K and 300 K and in high transverse field between 150 K and 200 K at PSI. NdPdAs has served as a reference system having an integral valence, the same crystal structure and a similar unit cell size. In this compound the trivalent Nd^{3+} ($^4\text{I}_{9/2}$) shows a Curie–Weiss-behaviour with an effective magnetic moment of $\mu_{\text{eff}} = 3.47\mu_{\text{B}}$ which is close to $3.62\mu_{\text{B}}$, the calculated free ion value. The paramagnetic Curie temperature is $\Theta = -9.8$ K. A magnetic transition is found at ≈ 15 K. From magnetization a dominantly ferromagnetic coupling is concluded.

In the paramagnetic regimes the ZF spectra of both systems show a strong signal with an exponential muon relaxation which could not be decoupled in longitudinal fields up to 0.2 T and an additional small signal ($\approx 1/5$ of the sample amplitude) with low static and temperature independent damping. The small signal will be ignored in this paper.

The ZF relaxation rate (fig. 1(a)) in NdPdAs shows a constant increase below 200 K reflecting the slowing down of the magnetic moments over a wide temperature range down to 15 K where the relaxation rate exhibits a maximum. The Moriya-type [6] high temperature limit of the muon relaxation can be estimated to $\approx 0.14(4) \mu\text{s}^{-1}$ where the relaxation rate levels off above 250 K. Additional 0.02 T TF measurement shows nearly identical relaxation rates. The dynamic nature of the muon relaxation proves that the nuclear damping mainly due to ^{75}As can be ignored for this signal.

In EuPdAs the dynamic ZF relaxation rate is $0.95 \mu\text{s}^{-1}$ already at 250 K and increases only slightly to $1.0 \mu\text{s}^{-1}$ at 50 K (fig. 1). This nearly temperature independent muon relaxation rate is a consequence of a stronger dipolar coupling (due to the 2.13 times larger magnetic moment in comparison to the Nd-system) and additional hyperfine coupling to the pure $L = 0$ state of the 4f electrons in Eu^{2+} . This muon relaxation behaviour is similar to Gd^{3+} -systems [7,8] where the rare earth has the same electronic 4f-state. Only below 50 K the relaxation rate increases more strongly

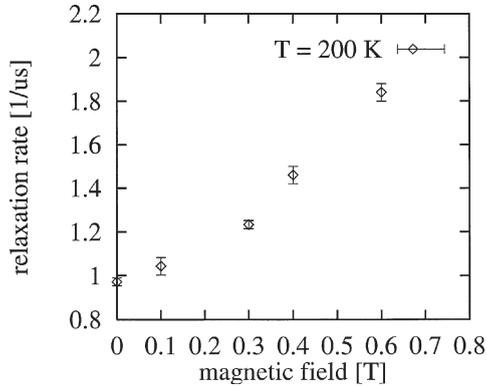


Fig. 2. Field dependence of the TF relaxation rate in EuPdAs at 200 K.

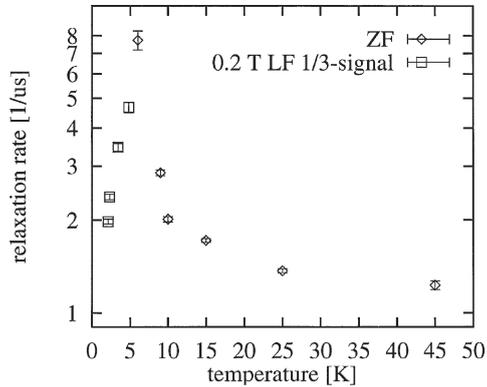


Fig. 3. Low temperature ZF and LF relaxation rates in EuPdAs.

due to a critical slowing down of the spin fluctuations above the magnetic transition at 5 K (fig. 3).

In the TF experiments a mean polarisation of the paramagnetic spins is achieved by applying an external magnetic field and the formation/deformation process of the Eu^{2+} spins induces a *time dependence* of the transverse field distribution at the muon site causing an averaged field distribution with a medium line width between the static widths of the different muon surroundings. In the EuPdAs system the TF measurements show a single frequency with increased relaxation rates. Because of the strong damping a systematic Knight shift behaviour could not be observed. The reason for this behaviour can be twofold. The powder broadening effect in this material is expected to be twice as large as in the neodymium compound because of the larger magnetic moment of the Eu^{2+} . If the dipolar interaction would dominate over the hyperfine coupling its anisotropy causes a continuous range of negative as well as positive Knight shifts at the muon site depending on the angle between the temperature and field dependent paramagnetic polarisation, which is parallel to the external field,

and the individual crystal c -axis. Therefore even a fully static valency distribution would not result in separated resonance lines in the μ SR spectrum of polycrystalline samples. Instead one would expect a sum of resonance lines with different widths centered nearly at the same frequency. The intensity of these signals will be proportional to the probability of the corresponding muon surrounding. Only in this way a change in the mean valence would alter the observed frequency spectrum. Figure 2 shows the field dependence of the transverse relaxation rate in EuPdAs at 200 K. In a linear regression a slope of $\approx 1.5 \mu\text{s}^{-1}/\text{T}$ is obtained, which is only 1/10 of a calculated value assuming pure dipolar coupling to two nearest neighbour Eu^{2+} spins. We conclude that the dipolar coupling strength is low and the dominant interaction is isotropic hyperfine coupling. In the dynamic limit of the valence fluctuation regime a quadratic field dependence of the TF relaxation rate is expected. Assuming a Knight shift difference of 1% between the different muon surroundings a quadratic fit of the field dependence results in a valence fluctuation rate of $\nu_{\text{VF}} \approx 0.8 \mu\text{s}^{-1}$. This value should be considered as an estimate only since it depends quadratically on the not explicitly known Knight shift difference. Nevertheless, it is in agreement with the Mössbauer results.

The small step in the TF relaxation rate at the valence transition at 170 K is a consequence of the accompanying 3% reduction of the c -axis lattice parameter which enhances the muon Knight shift.

Below 50 K the critical slowing down process of the residual Eu^{2+} spins dominates the muon relaxation and the relaxation rate diverges at 5 K (fig. 3). At lower temperatures a small signal fraction could be recovered in 0.2 T longitudinal field. This is interpreted as the 1/3-tail of a nearly static ZF relaxation function with a broad static width of the internal field distribution of the order of 0.5 T and indicates indeed a non-collinear magnetic structure in these systems.

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