

Muon Knight-shift measurements in CeSn_3 and some isostructural rare-earth compounds

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The muon Knight shift K_μ is studied as a function of temperature in CeSn_3 , CePd_3 , CeIn_3 , LaSn_3 , LaPd_3 , LaIn_3 , PrSn_3 , and PrIn_3 . K_μ can be regarded as a measure of the local susceptibility at the muon site. The data are discussed in reference to the bulk susceptibility. Anomalous K_μ contributions in CeSn_3 and CePd_3 are attributed to an enhanced d character of the conduction electrons in these mixed-valence systems.

Positive muons, stopped in a solid, come to rest at interstitial sites, where the muon spin performs a Larmor precession in the local magnetic field. The muon Knight shift is then a measure of the local magnetic susceptibility. By studying a series of isostructural rare-earth compounds we try to separate the contribution of the $4f$ states to the μ Knight shift. Compounds with well localized $4f$ states, PrIn_3 , CeIn_3 , and PrSn_3 , will be compared with intermediate-valence systems,¹ CeSn_3 and CePd_3 , and the nonmagnetic references LaIn_3 , LaSn_3 , and LaPd_3 .

Polycrystalline samples were prepared by arc melting followed by an annealing in a high-frequency furnace. X-ray diffraction showed no lines other than those of the Cu_3Au structure with the usual sensitivity limit of 5%. The samples were shaped to spheres of about 20-mm diameter by spark cutting. The muon experiments were carried out in a transverse magnetic field of 3.7 or 7.4 kG using a stroboscopic method² which allows a high data-collection rate necessary for a precise determination of the muon Larmor frequency ω_μ . As usual the muon Knight shift is defined as $K_\mu = (\omega_\mu/\omega_0) - 1$, where ω_0 is the muon Larmor frequency in vacuum.

From volume considerations it is most likely that the muon preferentially occupies the octahedral interstices of the Cu_3Au structure—as it does in metals with the closely related fcc structure³—rather than the tetrahedral sites. There are, however, two nonequivalent octahedral sites, one with a noncubic point symmetry, so that in principle two resonances are expected. In the present experiments we observed only one resonance because either the muon performs a site average by fast diffusion or the frequency difference is small with respect to the apparent width of the signal which is given by the muon lifetime and the intrinsic width Γ . The signals were thus fitted by a single resonance yielding the quantities K_μ and Γ .

The results on the Knight shift as a function of temperature are shown in Fig. 1 for CeSn_3 , LaSn_3 , LaIn_3 , and PrSn_3 , and in Fig. 2 for LaPd_3 and CePd_3 . The limited data on CeIn_3 and PrIn_3 obtained so far are listed in Table I. The parameter K_μ is positive for the Sn and In compounds and negative for the Pd compounds. There is a maximum of $K_\mu(T)$ in CeSn_3 and CePd_3 between 150 and 200 K. The

Knight shift of CeSn_3 falls below the values of LaSn_3 at a temperature of about 50 K. The Knight shift of CePd_3 is at all temperatures investigated more negative than that of LaPd_3 .

The value of the method in the present context depends on whether it really probes intrinsic properties of the crystal or whether the muon spin is rather precessing at irregular sites of the specimens like grain boundaries. Some insight into the selection of sites can be obtained from the width Γ

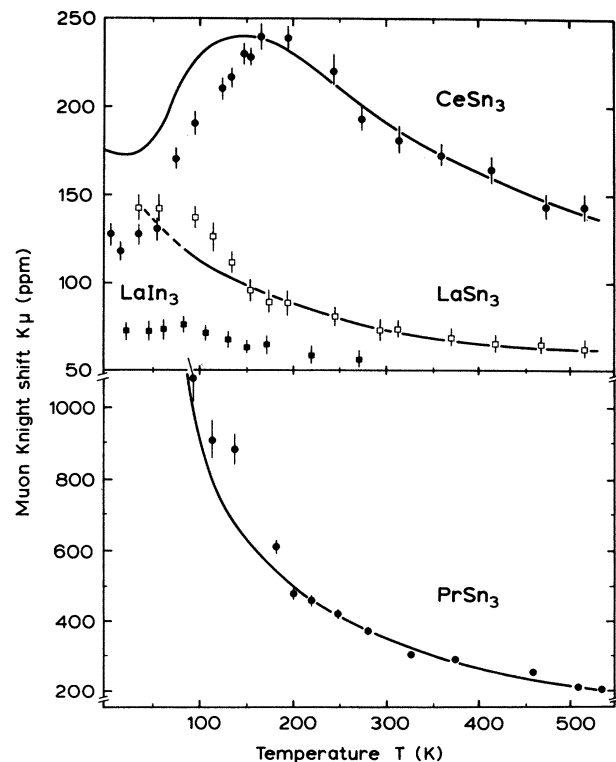


FIG. 1. Muon Knight shift of CeSn_3 , LaSn_3 , LaIn_3 , and PrSn_3 as a function of temperature. The solid lines refer to bulk magnetic susceptibility data.

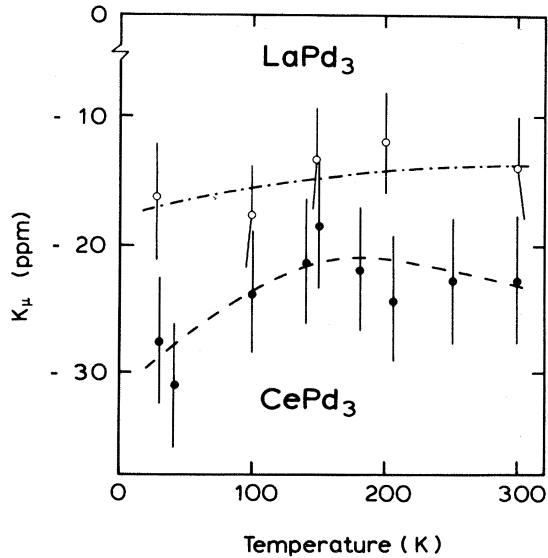


FIG. 2. Muon Knight shift of LaPd_3 and CePd_3 as a function of temperature. The lines are guides to the eye.

of the resonance signal. LaIn_3 may serve as an example. Here Γ is about 0.16 MHz below 100 K, and it decreases with increasing temperature following roughly an Arrhenius law reaching a room-temperature value of 0.03 MHz. The low-temperature value is in excellent agreement with the calculation of the second moment of dipole fields originating from the nuclear La and In moments, averaged over the two inequivalent octahedral interstitials. Thus the linewidth results are consistent with the muons residing in regular interstitials at low temperatures and a motional narrowing of the line due to a thermally activated process like muon diffusion.

From the figures it is obvious that the temperature dependence of the Knight shift is closely related to the temperature dependence of the bulk susceptibility χ_B , which is well known for the systems under study. Since the MHz frequencies of the μ precession are small compared to the characteristic frequencies of the electron system one can ignore the dynamic aspect of the experiment and compared K_μ with static susceptibilities. The results are thus analyzed in terms of the linear expression $K_\mu(T) = K_0 + B_{\text{hf}}\chi_B(T)$. The coefficient B_{hf} can be understood as a muon hyperfine field which is a measure of the extent to which the spatially averaged magnetization of the sample is experienced by the muon's magnetic moment at the interstitial site. For practical reasons one is inclined to distinguish contributions to K_μ

from different types of electrons according to

$$K_\mu = \sum_i K_\mu^i = \sum_i B_{\text{hf}}^i \chi_B^i, \quad i = \text{"s," "d," and "4f"},$$

where "s" stands for wide-band electrons, "d" for narrow-band electrons, and "4f" for the localized 4f electrons. The experimental and theoretical base for this procedure is not firmly established, although one knows from simple metals that the muon couples to the paramagnetic and diamagnetic susceptibilities of quasifree conduction electrons with hyperfine fields of the order of 50 kG/ μ_B via the Fermi contact field.³ The coupling to 4f is weaker, B_{hf}^{4f} is nearly two orders of magnitude smaller, due to the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism.⁴ The d-electron effects are intermediate in strength. B_{hf}^d may be even negative as was shown by a systematic study on $\text{LaAg}_{1-x}\text{In}_x$ where the d contributions could be varied by alloying.⁵ A sound understanding of the negative hyperfine fields is still missing. It is the merit of the μ Knight shift that it probes the magnetization of the sample with spatial weights different from a susceptibility measurement.

We first concentrate on the results on the La compounds. The rather large shifts of LaSn_3 and LaIn_3 when compared to $\text{La}_{0.74}\text{Th}_{0.26}$ (Ref. 4) suggest that a considerable proportion of wide band electrons, which contribute to K_μ via the positive Fermi contact field, results from the nontransition metals Sn and In, respectively. A support for this statement comes from the observation that the shift in LaSn_3 is larger than in LaIn_3 which is explained by the larger number of valence electrons of Sn compared to In. Actually the electronic density of states at the Fermi level as deduced from specific-heat measurements $N(E_F)$ is 0.65 and 0.4 (states/eV unit-cell-spin) for LaSn_3 and LaIn_3 , respectively,⁶ and we note that the ratio $N(E_F)/K_\mu$ at 300 K is about equal for the two compounds. On the other hand, the temperature dependence of K_μ suggests that non-s-like states are present at the Fermi level in these systems. In particular, the Knight shift in LaSn_3 shows a strong temperature dependence similar to the bulk susceptibility χ_B (though there are noticeable differences between the data of different authors). A fit to the linear K_μ - χ_B relation (χ_B is taken from Ref. 7) yields a temperature-independent Knight-shift part $K_0 = 20$ ppm and a positive hyperfine field $B_{\text{hf}} = 1.6$ kG/ μ_B (solid line in Fig. 1). Since the exact origin of B_{hf} is yet unclear this type of analysis may be somewhat artificial; nevertheless, the data support the view that a temperature-dependent magnetization component exists in LaSn_3 .

In LaPd_3 we note a small negative, weakly temperature-dependent Knight shift. The negative value is consistent with the diamagnetic susceptibility observed in this com-

TABLE I. μ -Knight-shift values of CeIn_3 and PrIn_3 (in ppm).

T	200 K	220 K	240 K	260 K	300 K	330 K
K_μ (CeIn_3)	112(5)	98(6)	97(5)	90(4)	87(4)	80(4)
K_μ (PrIn_3)	460(15)	...	430(12)	...	375(8)	...

pound.⁸ Presumably the contribution from wide-band electrons at the μ site is small and overcompensated by negative hyperfine fields originating from d -like Pd electrons. These d -like electrons might also be responsible for the residual T dependence of K_μ , a view which is further supported by the result that in pure Pd a strong negative T -dependent Knight shift of about -100 to -300 ppm was observed between room and helium temperatures.⁹ Thus narrow-band electrons have an increased importance in LaPd₃ relative to the other two La compounds.

CeIn₃ and the two Pr compounds are representatives of paramagnetic systems with local trivalent $4f$ states since their bulk susceptibilities follow well Curie-Weiss laws with the Curie constants of the trivalent ions.¹⁰⁻¹² In PrSn₃ a large additional polarization of the conduction electrons from the local $4f^2$ moments of Pr. The muon Knight shift follows the Curie-Weiss-type behavior of the bulk susceptibility $\chi_B(T)$ which is shown in Fig. 1 as a solid line. Since the susceptibility of the Pr ions χ_{4f} is by far the dominant part of χ_B one may identify B_{hf} with the induced hyperfine field per $4f^2$ moment. We obtain from a fit to the linear K_μ - χ_B relation $B_{\text{hf}}=0.36$ kG/ μ_B , $K_0=25$ ppm. The same procedure applied to the data on CeIn₃ and PrIn₃ yields $K_0=20$ ppm and $B_{\text{hf}}=0.17$ kG/ μ_B for CeIn₃ and $K_0=20$ ppm and $B_{\text{hf}}=0.35$ kG/ μ_B for PrIn₃ although these figures are less accurate. These low values of the hyperfine field suggest that the magnetization of the $4f$ states is, in fact, transferred to the μ site by the indirect RKKY exchange. The exchange constant J_{sf} is estimated⁴ to be of the order of -0.1 to -1 eV.

In the Curie-Weiss regime of CeSn₃ (Refs. 10 and 13) above 200 K a fairly large hyperfine field B_{hf} compared to the former values is deduced from the linear relation between $K_\mu(T)$ and $\chi_B(T)$; namely, $B_{\text{hf}}=0.52$ kG/ μ_B , $K_0=30$ ppm. Actually the muon Knight shift in CeSn₃ above 200 K is about twice as large as the corresponding shift in CeIn₃.

In the intermediate valence regime of CeSn₃ the local magnetization as experienced by the muon decreases more strongly below 200 K than the magnetization of the $4f$ state as deduced from the bulk susceptibility.¹³ This behavior reflects either a modification of the transferred hyperfine fields between the $4f$ moments and the muon or signals the influence of an additional negative Knight-shift contribution which was absent or small in the high-temperature range.

As has been mentioned before, a similar anomaly occurs in the ¹⁹⁹Sn-NMR Knight shift in CeSn₃.¹⁴ However, the sign of the NMR anomaly (increase of B_{hf}) is opposite to the muon results (decrease of B_{hf}). Following the possibility of a changed transfer mechanism one derives a hyperfine field of 0.40 kG/ μ_B (assuming that K_0 is unchanged) which is 25% lower than the field in the Curie-Weiss regime.

In CePd₃ the relative errors of K_μ are too large to warrant a reliable linear fit. Nevertheless, B_{hf} should have a positive value since both $K_\mu(T)$ and $\chi_B(T)$ exhibit maxima at about 180 K. CePd₃ is considered to be a valence fluctuator throughout the temperature range of the present study. One can summarize the results on CeSn₃ and CePd₃ by noting that in the regime of valence fluctuations K_μ is more negative than in the corresponding La-reference compound. The anomalous reduction of K_μ might be regarded as an indication for additional negative d -electron Knight-shift contributions. In terms of a band picture, which is at least for CeSn₃ strongly supported by de Haas-van Alphen measurements,¹⁵ the increase of d character at the Fermi level can be understood as a $4f$ - $5d$ hybridization effect. It is clear that in such a case the application of the RKKY approach, which is based on the assumption of a localized $4f$ electron, is questionable. Presumably the negative K_μ contributions can be attributed to the e_g subband, since according to Liu *et al.*¹⁶ the e_g and t_{2g} components of the Ce $5d$ electrons play a different role in the crystal bonding of CeSn₃. The crystal bonds between the Ce and the Sn atoms are preferentially formed by the Ce $5d(t_{2g})$ and the Sn $5p$ orbitals while the Ce $5d(e_g)$ orbitals are weakly coupled. Therefore, the hybridization of the $4f$ state with the $5d$ - e_g orbitals causes less disruption of the crystal bonds and is hence preferred. Pertaining to the muon experiments we note that muons occupying those octahedral sites with four metallic and two rare-earth first neighbors should be particularly sensitive to variations in the $5d$ - e_g states as is obvious from the symmetry of these orbitals.

In summary, we have shown that in systems with stable $4f$ shells the μ Knight shift follows the bulk susceptibility with relatively small coupling coefficients which signal that the $4f$ polarization is in fact transferred to the μ site by an indirect mechanism. In the intermediate valence regime anomalous, negative Knight-shift contributions appear which are presumably due to an enhanced d character of the conduction electrons.

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