Investigation of the γ-to-α phase transition of Ce and $Ce_{0.74}Th_{0.26}$ by muon spin rotation

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Positive muons have been used as a local probe of the polarization of the conduction electrons in the γ and in the α phase of Ce and $Ce_{0.74}Th_{0.26}$. Whereas the muon Knight shift in the $4f$-free reference system $La_{0.74}Th_{0.26}$ is temperature independent and almost zero, the shift in the γ phase of Ce and Ce-Th is positive and reflects the temperature dependence of the bulk susceptibility. The results are discussed in terms of an indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction between the local $4f$ electrons and the conduction electrons. In the collapsed α phase the proportionality constant between the muon Knight shift and the bulk susceptibility remains nearly unchanged indicating that the $4f$ electrons attain only little itinerant character upon the transition. The anomalies, both in the Knight shift and in the linewidth, of the muon signal observed around the γ-to-α transition temperature are presumably connected with the divergent elastic response.

I. INTRODUCTION

fcc cerium exists in two phases, the γ and the α phase. The cell volume of the α phase is about 16% lower than that of the γ phase. At room temperature the transition to the collapsed phase occurs at a pressure of 8 kbar. Similar to the liquid-gas system, the phase separation line terminates at a critical point, which is at $T_c = 600$ K, $P_c = 20$ kbar.[1] The γ-to-α transition is also observed in $Ce_{1-x}Th_x$ alloys. Here the Th concentration can be regarded as being equivalent to a pressure. The phase separation line ends at $T_c = 150$ K and a critical concentration $x_c = 0.269$ at zero applied pressure.[2]

The contraction of the lattice is connected with a change of the magnetic susceptibility from a Curie-type behavior to a temperature-independent behavior.[3,4] The transition was explained by a delocalization of the $4f^1$ electron. In the γ phase the Ce ions exist in the usual tripositive valence state of the rare-earth ions, giving rise to ionic magnetism, whereas in the α phase the Ce ions are formally tetravalent, nonmagnetic, and the former $4f$ electron is converted into a band electron. The exact nature of this conversion is still a matter of discussion; the electron may be either promoted to the (s,d) bands or may attain dispersion on its own via a Mott transition.[5]

In recent years muon spin rotation (μ^+SR) has been developed as a new research method in solid-state physics. The positive muon can be used as a probe of the local magnetic fields at an interstitial site of the lattice.[6] In particular, the muon feels the polarization of the conduction electrons via the Fermi contact field. Thus one can hope to obtain further insight into the γ-to-α transition by application of μ^+SR. The γ-to-α transition offers the chance, so to speak, to change the number of the conduction electrons, and it was the purpose of the present investigations to find out if the delocalized $4f^1$ electrons in the α phase give rise to direct contributions to the muon Knight shift.

We report muon Knight-shift studies on Ce and $Ce_{0.74}Th_{0.26}$ and on the $4f^1$-free reference system $La_{0.74}Th_{0.26}$. First we give a short outline of the experimental procedure; the Knight-shift results are presented in Sec. III. In Sec. IV special attention is paid to the diffusion behavior of the muon in order to confirm that the temperature dependence of the Knight shift is not masked by trapping and site change effects of the muon. Anomalies both in the Knight shift and in the relaxation rate of the muon signal near the γ-to-α-transition temperature are discussed in Sec. V. Finally we compare our experimental results with current theories on the behavior of the $4f$-electrons upon the transition.

II. EXPERIMENTAL

Polycrystalline Ce, $Ce_{0.74}Th_{0.26}$, and $La_{0.74}Th_{0.26}$ samples were prepared by high-frequency melting in a cold crucible. The starting materials Ce, La, and Th were 99.99% pure. The La-Th and the Ce sample were machined to spheres 20 mm in diameter. The Ce-Th sample had the shape of an ellipsoid with the axes (a,a,c) and $c/a=0.5$. The samples were annealed under vacuum for one week at 700 K. The fcc crystal structure was verified by neutron diffraction. The temperature dependence of the lattice constant of Ce-Th was found to agree with the values reported in the literature.[7]

The α phase of pure Ce was reached by cooling a separate, disk-shaped (25×5 mm^2) Ce sample down to liquid-nitrogen temperature under a pressure of 10 kbar and then releasing the pressure. By this procedure the formation of the β phase was circumvented.

The μ^+SR experiments were carried out on the high-precision stroboscopic instrument at the SIN in a transverse field of 7.4 kG which corresponds to a Larmor frequency of the muon of about 100 MHz. A complementary measurement on Ce-Th was performed with a conventional μ^+SR setup in a transverse field of 200 G using the time differential method.

For the spherical samples no demagnetization corrections were necessary since demagnetization field and Lorentz field cancel. The corrections for the ellipsoidal Ce-Th sample and for the disk-shaped α-Ce sample were determined experimentally rather than by calculation. At several temperatures the local field B_μ at the muon was measured both with the long and with the short axes of the samples parallel to the external field B_0. The Knight shift K is then obtained from

$$K=\frac{2B_\mu^{\text{long}}+B_\mu^{\text{short}}}{3B_0}-1 \ .$$

III. KNIGHT SHIFT

The Knight-shift results are shown in Figs. 1 and 2. In the $4f^0$ reference system La-Th—see Fig. 2—the shift is temperature independent and almost zero. Obviously the positive contribution $K_+^p(R_\mu)$ which is due to the Fermi contact field at the muon at R_μ, into which the Pauli paramagnetic susceptibility χ_p and the conduction-electron density at the muon site enter, is cancelled by negative contributions $K_-(R_\mu)$ which we attribute mainly to a diamagnetic shielding of the muon. In simple metals values for the diamagnetic contributions typically between -20 and -30 ppm have been calculated.[9,10] The total Knight shift of the muon in La-Th may thus be written symbolically:

$$K(R_\mu)=K_+^p(R_\mu)+K_-(R_\mu) \ . \quad (1)$$

In γ-Ce and in Ce-Th positive values of K were observed over the whole temperature range which

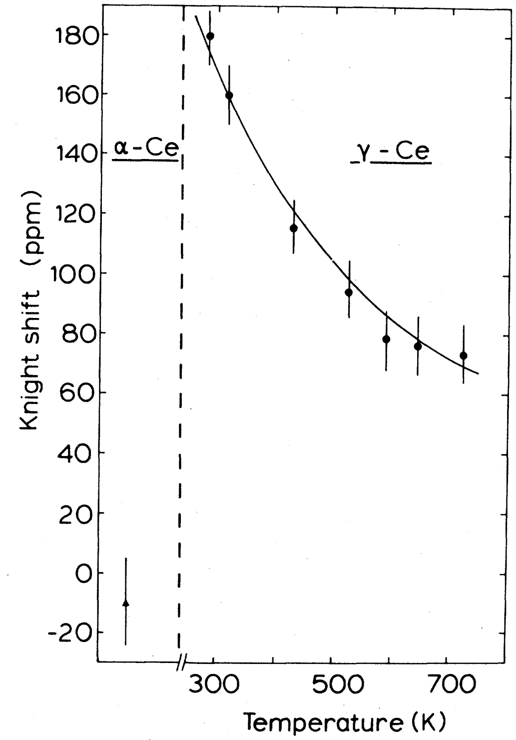

FIG. 1. The muon Knight shift in γ-Ce and α-Ce as a function of temperature. The light solid line gives the bulk susceptibility taken from Ref. 8 after appropriate scaling to fit the Knight-shift data.

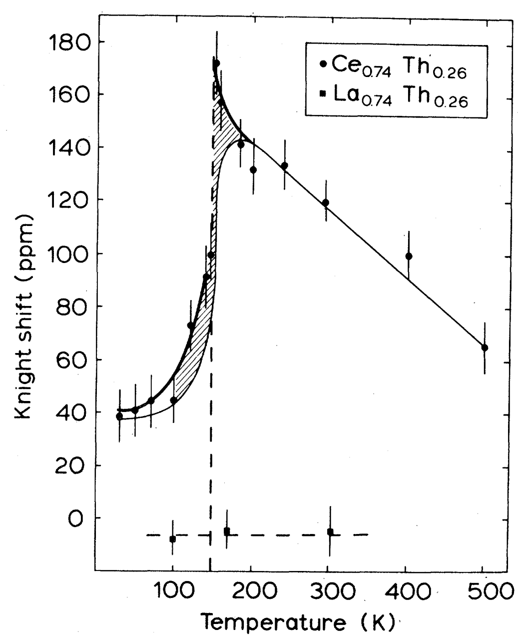

FIG. 2. The muon Knight shift in $Ce_{0.74}Th_{0.26}$ and $La_{0.74}Th_{0.26}$ as a function of temperature. The dotted line and the heavy solid lines are guides to the eye. The light solid line gives the bulk susceptibility χ_B taken from Ref. 3. χ_B is scaled to fit the data at high temperatures.

was accessible in the present study. In γ-Ce and in γ-Ce-Th, well above the transition temperature T_s, the data follow within the experimental error the Curie-type behavior of the bulk susceptibility $\chi_B(T)$. The linear relation is demonstrated in Fig. 3—circles—where $K(T)$ is plotted versus $\chi_B(T)$. We propose to interpret this result by a polarization of the conduction electrons at the muon by the local $4f^1$ moments at the regular lattice sites R_i via the Ruderman-Kittel-Kasuya-Yosida (RKKY)-exchange interaction. Assuming for simplicity that the conduction electrons at the interstitial muon have only free-electron character, the Knight shift in the γ phase can be written in the well-known form[11]

$$K_\gamma(R_\mu,T)=K_+^p(R_\mu)\left[1+6\pi Z\frac{(g_J-1)}{g_J\mu_B^2}J(0)\chi_{4f}(T)\sum_i F(2k_F|R_\mu-R_i|)\right]+K_-(R_\mu) \ , \tag{2}$$

where $\chi_{4f}(T)$ is the susceptibility of the $4f$ ions, $J(0)$ is the zero wave-vector exchange constant of the RKKY-exchange interaction, Z is the number of conduction electrons per atom, and the other symbols have their usual meaning. If a uniform polarization model is adopted it is common practice to define a phenomenological exchange constant via: $J_{sf}=-6\pi ZJ(0)\sum_i F(2k_F|R_\mu-R_i|)$. In the more realistic case $K(R_\mu)$ depends on the actual muon site. If for example, in pure Ce, the muon resides exclusively on octahedral interstitial sites, K would have an unique value. In the alloy one expects a distribution due to the variation of the local environment. If the muon is diffusing rapidly, an assumption which will be justified in the next section, one may perform a site average over the sample and Eq. (2) is transformed to give the mean value of the Knight shift as

$$K_\gamma(T)=A_\gamma\chi_B(T)+(K_+^p+K_-) \ , \tag{3}$$

where the coefficient A_γ scales with the Ce concentration and the last term corresponds to the Knight shift in the absence of the $4f$ moments. Introducing little error we have identified $\chi_B(T)$ with $\chi_{4f}(T)$.

Experimentally (see Fig. 3) one observes for γ Ce-Th an almost vanishing offset $(K_+^p+K_-)$, in good agreement with the result on the background system (La, Th) and $A_\gamma=0.35$ kG/μ_B. For γ-Ce, we find $(K_+^p+K_-)=-20$ ppm and $A_\gamma=0.46$ kG/μ_B. Thus A_γ scales roughly with the Ce concentration which is a strong indication that the major part of the Knight shift is due to the exchange mechanism. Provided that K_+^p has a value of about +30 ppm [from Eq. (1)] we then obtain for the constant J_{sf} the values −0.8 and −1.1 eV in the case of Ce-Th and Ce, respectively. However, considerable error perhaps up to 50% may enter into the absolute value of J_{sf} because of the uncertainties introduced by the estimation of K_+^p.

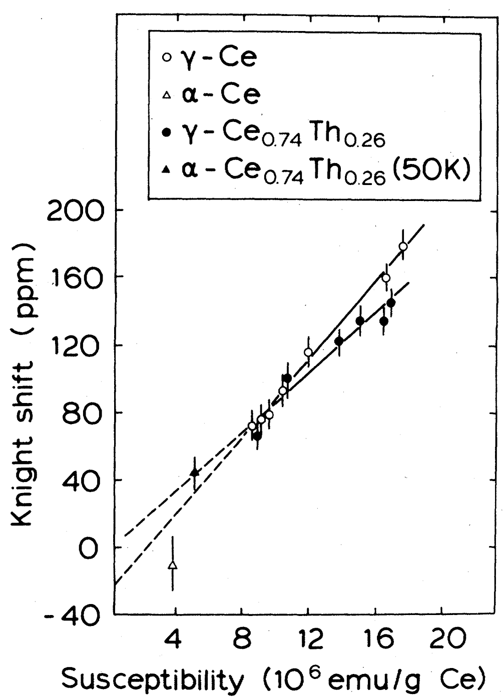

FIG. 3. Demonstration of the linear relation between the muon Knight shift and the bulk susceptibility in γ-Ce and γ-$Ce_{0.74}Th_{0.26}$ for temperatures above 180 K as implicit parameters. The α phase values are also shown.

In the α phase, far from the phase transition, it is generally assumed that the formation of the local $4f^1$-moments is suppressed or at least significantly reduced. Consequently the temperature-independent bulk susceptibility was interpreted as an enhanced Pauli spin susceptibility originating mainly from the former $4f$ electrons. Writing formally: $\chi_B=\Delta\chi+\chi_p$ where $\Delta\chi$ refers to the enhanced part of the susceptibility, one expects, in analogy to Eq. (3), the Knight shift to be given by

$$K_\alpha(T)=A_\alpha\Delta\chi+(K_+^p+K_-) \ . \tag{4}$$

If $\Delta\chi >> \chi_p$ one can approximate $\Delta\chi$ by the bulk susceptibility χ_B and again a linear relation between K and χ_B is obtained. We note that within the experimental error the values A_γ and A_α are identical for Ce, respectively, Ce-Th (Figs. 2 and 3). This observation will be interpreted in the final section. Significant deviations from the linear relation between $K(T)$ and $\chi_B(T)$ were observed in Ce-Th around the γ-to-α transition temperature (Fig. 2) which will be discussed later.

IV. LINEWIDTH

One has to confirm that the temperature behavior of the muon Knight shift, which was attributed to the temperature dependence of the $4f$ spin susceptibility, is not masked by diffusion and trapping effects of the muon. If, for example, in a certain temperature range the muon resides exclusively at irregular sites, like grain boundaries then K will differ from its value for regular interstitial sites.

Information about the diffusion behavior of the muon can be obtained from the relaxation rate of the muon signal. In addition the linewidth should reflect structural and critical effects connected with the γ-to-α phase transition.

The results of the intrinsic linewidth Λ of the resonance, which is the reciprocal transverse relaxation time T_2^{-1}, are shown in Fig. 4.

The linewidth is due to distributions of the local field at the muon site. In the present sample the field is partially a dipolar field which originates from the surrounding atomic moments and from the nuclear spins. In addition the indirect exchange field acts on the muon.

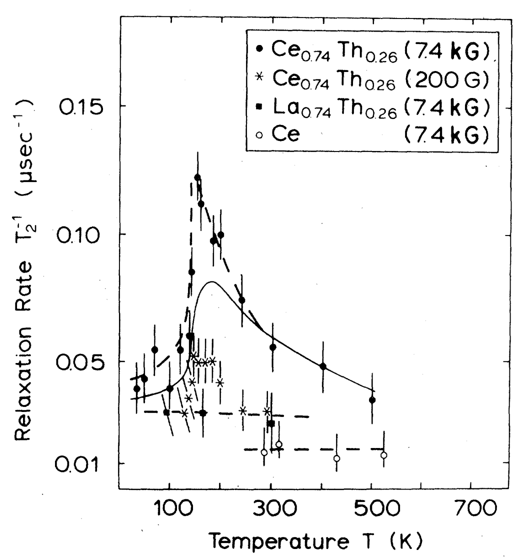

FIG. 4. The transverse muon spin relaxation rate Λ in Ce and in $La_{0.74}Th_{0.26}$ at 7.4 kG and in $Ce_{0.74}Th_{0.26}$ at 7.4 kG and 200 G as a function of temperature. The dotted lines are guides to the eyes. The solid line gives the expression $[\chi_B(T)B_0/R(T)^3]^2$ as defined in the text, after appropriate scaling to fit the data above 200 K and below 100 K.

The local environment of the muon plays an important role. In a fcc lattice the muon is expected to occupy the octahedral interestitial sites.[12,13] In the fcc-type alloys, La-Th and Ce-Th even these interstices have a noncubic point symmetry due to the statistical substitution of La or Ce by Th ions. Thus the octahedral interstices of the alloy are nonequivalent. We have to discriminate between the line-broadening effect of the static-induced components of the randomly distributed magnetic moments—which are oriented along the applied field and which scale with it—and the effect of the full fluctuating moments.

We first concentrate on the results of La-Th. The $4f$ free reference system shows a finite temperature-independent linewidth between 100 and 300 K. Since the local hyperfine fields at the muon are expected to be always small the field distributions are mainly generated by the nuclear moments of La. A calculation of the second moment for a muon in an octahedral interstice with a statistical occupation of the surrounding lattice sites by La and Th atoms predicts a linewidth of about 0.07 μsec^{-1}; the expected width for a muon at a tetrahedral interestitial site is about 10% larger, the width for a muon at a vacancy is about 30% smaller. The lower experimental values propose that a diffusive motion of the muon effectively narrows the linewidth. Thus we conclude that trapping effects, if they play a role in our samples at all, are temperature independent in the temperature range under investigation. As the nuclear moments of Ce and Th are considerably smaller than that of La, the nuclear dipolar width in Ce and in Ce-Th should be neglible.

Next we discuss the influence of the Ce moments. The apparent width of the resonance for pure Ce is almost entirely given by the muon lifetime, thus the intrinsic width is practically zero (Fig. 4). The fluctuating Ce $4f$ magnetic moments should in principle lead to a broadening of the resonance. The negative experimental result proposes that the $4f$ spin fluctuations are too fast to be sampled by the muon. In fact, spin-relaxation rates in the THz range have been determined from the quasielastic linewidth of the inelastic neutron spectrum in γ-Ce and γ-Ce-Th.[7,14]

The broadest resonances were observed in Ce-Th. The linewidth of this alloy was found to increase with falling temperature towards the γ-to-α transition. At T_s the maximum value of 0.12 μsec^{-1} was observed, below T_s the linewidth decays to a value of about 0.05 μsec^{-1} which is somewhat higher than the value of La-Th. The results of the complementary measurements at a low applied field exhibit significantly lower widths. From this fact and from the conclusions drawn for Ce and La-Th it is clear that the linewidth is related to the induced magnetic moments of the Ce ions. The reduced local symmetry of the muon sites in Ce-Th is essential in so far as the induced moments lead to nonvanishing local dipole fields and distributions of the exchange fields. From the Knight-shift results one may deduce that the relative variations of the exchange fields throughout the sample can be of the order of 100 ppm. The induced dipole fields can be calculated from the known bulk susceptibility and the lattice dimensions. We then expect Λ at 300 K to be of the order of 0.12–0.15 μsec^{-1} for a stationary muon at an octahedral site, which is again higher than the experimental value. In the case that the diffusion behavior of the muon is constant in the temperature range under investigation the muon spin-relaxation rate should scale with $(\chi_B(T)B_0/R(T)^3)^2$. The distance between the muon and the surrounding Ce ions has been written explicitly because of the strong temperature dependence of the lattice parameter. The solid line in Fig. 4 is the result of a linear fit of the experimental data to this expression for temperatures above 200 K and below 100 K very different from T_s. A good agreement is obtained but again deviations occur around T_s.

V. ANOMALIES IN Ce-Th AROUND T_s

In the vicinity of the transition temperature $T_s = 147$ K the linewidth and the Knight shift show considerably higher values than is expected from the otherwise linear relation with $(\chi_B(T)B_0/R(T)^3)^2$ and $\chi_B(T)$, respectively. The excess values of Λ and K around T_s are intimately connected with the phase transition which is first of all a lattice instability. The broadening of the linewidth may arise both from critical effects and from structural inhomogeneities which may occur during the collapse of the volume. First we comment on the influence of critical effects on the muon linewidth.

From neutron scattering experiments it is known that the $4f$-spin fluctuation rate, which is always high in the γ phase, increases at least by a factor of 3 in going to the collapsed α phase. Hence there is no critical slowing down of the $4f$ spin dynamics. However one has to discriminate between the lifetime of the $4f$ moment and the lifetime of the $4f$ configuration. Our recent ultrasonic measurements performed with sound waves of 10 MHz, which is roughly of the same order as the μ^+ Larmor precession frequency, have shown that the bulk modulus softens almost compeletely when T_s is approached and that the attenuation of the sound waves is very high in the wide temperature range $T_s \pm 30$ K.[15] Thus the γ-to-α transition can be regarded as an instability with respect to an A_{1g} breathing mode of the $4f^1$ orbit. The breathing motion accompanies the electronic configurational transition, e.g., the transition from a localized $4f^1$ state to a delocalized band state. Near T_s fluctuations between the two competing configurations are to be expected which should slow down when T_s is approached, freeze in at T_s and give rise to the γ-to-α volume collapse.

In the muon experiments the breathing motions of the $4f^1$ orbit can couple to the muon signal either via a modulation of the RKKY-exchange interaction and of the dipole interaction between the $4f$-moment and the muon spin or more directly via the electron charge density at the muon which enters K^{q}_{+} of Eq. (1)

Apart from critical fluctuations one also has to take into account the possible increase of lattice inhomogeneities during the large volume contraction. In the α phase untransformed γ-regions of the sample may exist, in particular, around lattice faults. However the fraction of trivalent Ce atoms in the α phase well below T_s must be small, since below 100 K the linewidth is not abnormally high.

Up to now it was supposed that the mobility of the muon remains unaffected by the γ-to-α transition. This assumption may be seriously in error if strain fields around lattice faults encourage the trapping of the muon during the lattice contraction. In this case one expects that Λ will be increased and K will be changed in an unknown way. The assumption of an increased trapping of the muon at lattice faults conflicts however with the experimental Knight shift results which seem to be systematically increased in the region where the susceptibility deviates from the Curie behavior. Obviously the reduction of the bulk susceptibility, which represents first of all the susceptibility of the $4f$ moments, and the small rise of the conduction electron polarization at the muon are closely related. If the assumption of the local $4f$ state and the application of the RKKY-exchange interaction are still satisfied close to the transition one quite generally expects that the value of the exchange integral between a local $4f$ electron and a conduction electron increases when the cell volume is reduced. Hence the local moment can be reduced at the expense of a compensating polarization of the conduction electrons.

VI. DISCUSSION

In most nonsimple metallic systems studied hitherto the muon Knight shift scales with the bulk susceptibility.[16] The merit of the muon experiments lies in the determination of the proportionality constant, which we called A. Since A specifies the density of the magnetic polarization at the muon site, which was supposed to be an interstitial site, relative to the spatially averaged density, the coefficient A can be regarded as a measure for the degree of localization of the electron spin density. In metals with quasifree and hence delocalized conduction electrons like the alkali and noble metals the muon experiences a local polarization which is enhanced as compared to the averaged polarization, the values of A are high, typically of the order of 50 kG/μ_B.[17] In lanthanide metals where the magnetic polarization is concentrated in the $4f$ orbitals, the polarization at an interstitial site due to the $4f$ moments can only be established by an indirect interaction, if—as it is the case in the present metals—the direct polarization of the conduction electrons at the muon is vanishingly small with respect to the average polarization. Hence the value for this situation is expected to be small. In fact A for γ-Ce and γ-Ce-Th is about two orders of magnitude smaller than in, e.g., in Cu.

In the α phase of Ce and Ce-Th it is expected that the magnetic polarization of the former $4f^1$ orbit is more extended as a consequence of the delocalization of the $4f^1$ electron, having perhaps a nonzero tail at the interstitial site. Hence the constant A should be increased with respect to its value in the γ phase. The experiments however show that the coefficient A is practivally unchanged by the γ-to-α transition. From this we conclude that the delocalization of the $4f$ electron upon the transition is only small without giving it the typical itinerant character of wide band electrons. Moreover the Knight-shift results do not provide experimental evidence against a description of the conduction electron polarization in the α phase in terms of an indirect interaction. In a recent electron band structure calculation Pickett *et al.*[18] have shown that the $4f$ state in the α phase might still be occupied by about one electron, the primary effect of the lattice contraction being a broadening of the f-bands and an increase of the $4f$ electron density midway between atoms. Our measurements support the idea of a $4f$-state occupation in the collapsed phase, an increase of the electron density at interstitial sites is not indicated.

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