Temperature and Field Dependence of the Order Parameter in the Antiferroquadrupolar Phase of CeB_6 from μ^+ Knight Shift Measurements

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(Received 21 July 2004; published 15 December 2004)

The Fermi contact hyperfine contribution to the Knight shift of positive muons, implanted at the interstitial $3d$ sites in CeB_6, is found to exhibit the same temperature dependence below T_Q in phase II as the quadrupolar order parameter determined from resonant and nonresonant x-ray scattering. Furthermore, the contact coupling parameter is shown to be anisotropic and field dependent. These unanticipated features are interpreted to arise from the RKKY induced conduction electron spin polarization, which depends on the orientation and expectation value of the ordered $4f$ quadrupole moments.

DOI: 10.1103/PhysRevLett.93.257601 PACS numbers: 76.60.Cq, 75.20.Hr, 75.25.+z, 76.75.+i

Ever since studies of the complex phase diagram of the dense Kondo system CeB_6 started about 25 years ago, this cubic compound has been the subject of continued experimental and theoretical investigations up to present days; some of the results are still under debate. CeB_6 crystallizes in the cubic CsCl-type structure, and the crystalline electric field splits the $4f^1\ ^2F_{5/2}$ multiplet into a Γ_7 doublet and a Γ_8 quartet, the latter being the ground state. What renders CeB_6 so interesting is the presence of multipolar (magnetic dipole-dipole, electric quadrupole-quadrupole, and magnetic octupole-octupole) interactions and their mutual interdependencies. The phase diagram consists of a low temperature double-$\mathbf{k}$ antiferromagnetic phase III [1,2] ($T_N \cong 2.3$ K in zero applied field H_{ext}, absent for $H_{\text{ext}} > 2$ T), followed by an antiferroquadrupolar (AFQ) phase II [propagation vector $\mathbf{q}_Q = (\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$] up to $T_Q = 3.2$ K at $H_{\text{ext}} = 0$ [1,3,4], and a paramagnetic Fermi liquid phase I above T_Q. In particular, phase II has attracted much attention due to the observation that application of $H_{\text{ext}} > 0$ induces an antiferromagnetic (AFM) dipolar order with $\mathbf{k}_{\text{AFM}} = (\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}) = \mathbf{q}_Q$ [1] and stabilizes phase II, as seen by the monotonic increase of T_Q with H_{ext} up to $\sim$10 K at 35 T [5]. This is now believed to originate from field induced magnetic octupole moments [6–8]. It was also concluded that at $H_{\text{ext}} = 0$ the quadrupolar order is of the Γ_5 type (i.e., O_{xy}, O_{xz}, O_{yz}) and for nonzero $\boldsymbol{H}_{\text{ext}} \parallel [001]$ of the O_{xy} type [7].

Meanwhile resonant and nonresonant x-ray scattering provided additional information on the AFQ order in phase II [9–11]. The temperature dependence of the order parameter p was found to follow the relation

$$p \propto (1 - T/T_Q)^{\beta} \tag{1}$$

with $\beta \simeq 0.33$–0.37 [9,10]. Lovesey [12] argued that the AFQ order is accompanied by a distorted CsCl structure (space group $Fmmm$), which preserves the cubic Ce sublattice but involves a change in the B_6 octahedron.

The transition from phase I to phase II is also well reflected in the Knight shift of positive muons (μ^+) implanted into CeB_6 [13,14]. This is *a priori* unexpected since the μ^+ is a local spin $-\frac{1}{2}$ probe sensitive to magnetic effects, but not to multipole features of the electric charge distribution in its vicinity. Moreover, as is discussed below, the anisotropic μ^+ Knight shift is found to be strongly field dependent in phase II, while, by definition, the Knight shift should be a field independent parameter. Previously the Knight shift was measured at only 6 kOe [14]. The peculiar results were interpreted on the basis of polarized neutron diffraction results, which were claimed to indicate an appreciable field induced magnetization density around the B_6 complex [15]. Since in the light of other work [16] this claim seems to be incorrect, the behavior of the μ^+ Knight shift must have another origin. In this Letter, we report on new extended measurements of the field and temperature dependence of the μ^+ Knight shift in phase II, partially motivated by the field and temperature dependence of the field induced staggered moment $\boldsymbol{m}_{\text{AFM}}$ as revealed by neutron diffraction [17]. The results facilitate a new and greater far-reaching understanding than previously possible.

From the high temperature μ^+ Knight shift it was concluded that the μ^+ are located at the interstitial $3d$ sites, $(\frac{1}{2}00)$, $(0\frac{1}{2}0)$, $(00\frac{1}{2})$ [14], situated rather symmetrically with respect to the nearest Ce neighbors, quite in contrast to the boron sites. As a consequence, the dipole and also the associated contact hyperfine (hf) fields from the field induced $\boldsymbol{m}_{\text{AFM}}$ cancel at the $3d$ sites and do not contribute to the μ^+ Knight shift. Also the type of transferred hf field present at the boron nuclei [18] is not expected at the μ^+.

The electronic structure at and around the μ^+ is given by the cloud of s-type conduction electrons screening the positive charge of the μ^+. Therefore the μ^+ will "see" only the dipole fields from the field induced ferromagnetically aligned moments $\boldsymbol{m}_{\mathrm{FM}} = \chi \boldsymbol{H}_{\mathrm{ext}}$ on the Ce sites and the contact hf field due to the spin polarization of the conduction electrons at the μ^+. The latter is induced also by the $\boldsymbol{m}_{\mathrm{FM}}$ via the RKKY interaction; χ is the isotropic bulk magnetic susceptibility due to the $4f$ electrons. Hence the μSR and the ^{11}B-NMR measurements probe the electronic and magnetic properties from a rather different and complementary perspective.

The muon spin rotation (μSR) measurements were performed at the Paul Scherrer Institute (PSI) making use of the low temperature instrument LTF and the general purpose spectrometer GPS on the πM3 beam line. In the GPS we used the same cylindrical sample as in Ref. [14]. Here we report only on measurements with $\boldsymbol{H}_{\mathrm{ext}} \parallel [001]$-axis. In the LTF we used a flat rectangular single crystal with the [001] axis perpendicular to the flat face and parallel to $\boldsymbol{H}_{\mathrm{ext}}$.

The transverse field μSR signal consisted of two well separated components (labeled 1 and 2) with an amplitude ratio of 2:1. This is to be expected because for the chosen arrangement the sites $(0\frac{1}{2}0)$ and $(\frac{1}{2}00)$ are magnetically equivalent but different from site $(00\frac{1}{2})$. The Knight shifts K_1 and K_2 were extracted from the fitted precession or Larmor frequencies by correcting for the demagnetization and Lorentz fields. Figure 1 shows some of the results for different fields as a function of temperature. The cutoff on the low temperature side is given by the onset of the antiferromagnetic phase III. Since phase III is absent at 25 kOe the Knight shifts could be measured down to 50 mK. The insets of Fig. 1 demonstrate that K_1 and K_2 ($H_{\mathrm{ext}} = 6$ kOe) scale with the bulk susceptibility χ for $T \geq 10$ K with slopes $dK_1/d\chi = 7.89(1)\ \mathrm{kG}/\mu_B$ and $dK_2/d\chi = -0.97(1)\ \mathrm{kG}/\mu_B$, independent of H_{ext}. We note [14] that both above and below T_Q $K_2(\boldsymbol{H}_{\mathrm{ext}} \parallel [110]) = K_1(\boldsymbol{H}_{\mathrm{ext}} \parallel [001])$, and that $K_2(\boldsymbol{H}_{\mathrm{ext}} \parallel [001]) - K_2(\boldsymbol{H}_{\mathrm{ext}} \parallel [110]) = 2\{K_1(\boldsymbol{H}_{\mathrm{ext}} \parallel [110]) - K_1(\boldsymbol{H}_{\mathrm{ext}} \parallel [001])\}$. This implies that the different $3d$ sites are crystallographically equivalent also below T_Q, precluding any sizable orthorhombic ($Fmmm$) distortion. Figure 1 demonstrates that K_1 and K_2 are field dependent, for $T < 10$ K and, most pronouncedly, below T_Q. This behavior seems to be closely related to the loss of scaling below 10 K.

Before discussing this issue we have to understand the measured slopes $dK_1/d\chi$ and $dK_2/d\chi$ above 10 K. The slopes for $\boldsymbol{H}_{\mathrm{ext}} \parallel [001]$ can be expressed as [14]

$$dK_1/d\chi = A_{\mathrm{con},1} - \tfrac{1}{2}A_{\mathrm{dip}}, \tag{2a}$$

$$dK_2/d\chi = A_{\mathrm{con},2} + A_{\mathrm{dip}}, \tag{2b}$$

where A_{con} is the contact hyperfine coupling and A_{dip} the appropriate dipolar coupling parameter. Assuming that A_{con} is isotropic (i.e., $A_{\mathrm{con},1} = A_{\mathrm{con},2}$) and temperature independent, one obtains from the slopes $A_{\mathrm{dip}} = 5.93\ \mathrm{kG}/\mu_B$. The calculated value for the $3d$ sites, however, is $3.94\ \mathrm{kG}/\mu_B$ [14]. This large discrepancy led to the model of Ref. [14], but since this model has lost its basis [16], the only alternative we can think of is to allow A_{con} to become anisotropic and temperature dependent, with A_{dip} given by the calculated value. This is confirmed by the observation that K_1 and K_2 pass through zero at certain temperatures below T_Q, which depend on H_{ext} (see Fig. 1). Generally, we can write

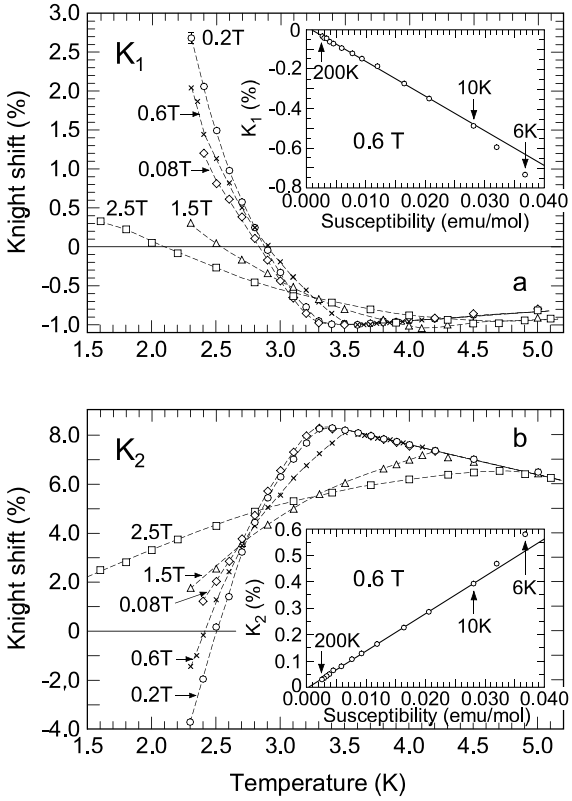

FIG. 1. Temperature dependence of the μ^+ Knight shifts (a) K_1 and (b) K_2 in CeB_6 in phase II at different fields $\boldsymbol{H}_{\mathrm{ext}} \parallel [001]$ axis. The insets show K_1 and K_2 plotted versus the magnetic susceptibility for $T \geq 6$ K and $H_{\mathrm{ext}} = 0.6$ T. Scaling is observed for $T \geq 10$ K.

$$K_i(T) = (A_{\mathrm{con},i} + \alpha_i A_{\mathrm{dip}})\chi(T) + K_{0,i}, \tag{3}$$

where $\alpha_1 = -\frac{1}{2}$, $\alpha_2 = 1$, and $K_{0,i}$ is a temperature independent contribution to the Knight shift. In the present case we find $K_{0,1} = 107(7)$ ppm and $K_{0,2} = -347(10)$ ppm. At the temperature T^*, where $K_i(T^*) = 0$, $(A_{\mathrm{con}} + \alpha_i A_{\mathrm{dip}}) = -K_{0,i}/\chi(T^*) \simeq 0$, and therefore $A_{\mathrm{con},i} \simeq -\alpha_i A_{\mathrm{dip}}$. This is possible only if A_{con} has become temperature dependent since A_{dip} does not depend on temperature as long as no site change occurs. Hence, above 10 K, A_{con} is temperature independent, but anisotropic [from Eq. (2) follows $A_{\mathrm{con},1} \equiv A_{\mathrm{con}}^{\perp} = 1\ \mathrm{kG}/\mu_B$ and $A_{\mathrm{con},2} \equiv A_{\mathrm{con}} = 3.95\ \mathrm{kG}/\mu_B$], and below 10 K it becomes also temperature dependent.

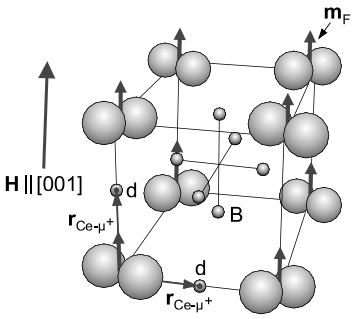

FIG. 2. Crystal structure of CeB_6 showing two magnetically inequivalent d sites, the field induced $\boldsymbol{m}_F = \chi \boldsymbol{H}_{ext}$ for $\boldsymbol{H}_{ext} \parallel [001]$, the two different distance vectors $\boldsymbol{r}_{Ce-\mu^+}$, and the $4f$ electron charge distribution in the O_{xy}-type AFQ ordered state (adapted from Ref. [8]).

Where appropriate, we use the superscripts $\perp, \parallel$ instead of $i = 1, 2$ to indicate that in the first case the vector $\mathbf{r}_{Ce-\mu^+}$, connecting the μ^+ and the two nearest Ce neighbors, is perpendicular and in the second case parallel to $\boldsymbol{m}_{FM}$ or $\boldsymbol{H}_{ext}$; see Fig. 2.

This brings us back to the loss of scaling. While this is usually attributed to a change of the local susceptibility χ_{loc}, possibly modified by the presence of the μ^+ [19], we find in the present case that it must mainly arise from the temperature dependence of $A_{con,i}$ and not from a modified χ_{loc}. Hence, with the assumption $\chi_{loc} = \chi_{bulk} \equiv \chi$, we can extract $A_{con,i}$ from K_i using Eq. (3), i.e.,

$$A_{con,i} = (K_i - K_{0,i})/\chi - \alpha_i A_{dip}, \tag{4}$$

where $A_{dip} = 3.94\ \mathrm{kG}/\mu_B$. To facilitate this calculation we have measured χ for all used fields $\parallel [001]$ axis, from 1.8 to 10 K using a quantum design physical properties measurement system. The resulting $A_{con}^{\perp,\parallel}$ for $H_{ext} = 25$ kOe are displayed in Fig. 3. Since the susceptibility measurements did not extend below 1.8 K, the assumed extrapolation renders the Lorentz and demagnetization corrections and the extracted A_{con} below 1.8 K somewhat uncertain. However, this is a problem only for the 25 kOe data. Figure 3 reveals the surprising feature that $A_{con}^{\parallel,\perp}$ is temperature independent in a small range above T_Q (and again above 10 K) and shows a very smooth temperature dependence below T_Q, which is reminiscent of the spontaneous magnetization in the ordered magnetic state. In fact, all data for $H_{ext} \geq 1$ kOe are excellently fitted in the range $T \leq T_Q$ by the equation

$$A_{con,i}(T) = A_{con,i}(0)[1 - (T/T_{Q,i})^{\gamma_i}]^{\beta} + A_{con,i}(T_Q), \tag{5}$$

with $\beta = 0.5$, $\gamma^{\perp} = 1$, and $\gamma^{\parallel} = 2$. This is demonstrated for $H_{ext} = 25$ kOe by the solid lines in Fig. 3. In this case the fit was restricted to the range $1.8\ \mathrm{K} \leq T_Q$ for the reasons mentioned above, but see also the caption of Fig. 3. However, for $H_{ext} = 500$ and 800 Oe better fits in terms of the normalized χ^2 were achieved by fixing $\gamma^{\perp} = \gamma^{\parallel} = 1$ and freeing β. The overall quality of the fits is demonstrated in Fig. 4, where we plot $\delta A_{con,i} = A_{con,i} - A_{con,i}(T_Q)$ versus T/T_Q, including the fitted curves. The best fit parameters $A_{con,i}(0)$, β, and $T_{Q,i}$ are collected in Table I. As the table shows, the fitted parameters depend rather weakly on H_{ext}, except, of course, T_Q. The obtained "simple" temperature dependence of $A_{con}^{\perp,\parallel}$ is taken as an indication that our assumption $\chi_{local} = \chi_{bulk}$ is basically right, at least down to 1.8 K. Quite reasonable fits for $A_{con}^{\parallel}$ could also be achieved by generally fixing $\gamma_i^{\parallel} \equiv 1$ and freeing β; this reduced $\beta^{\parallel}$ to values between 0.4 and 0.44.

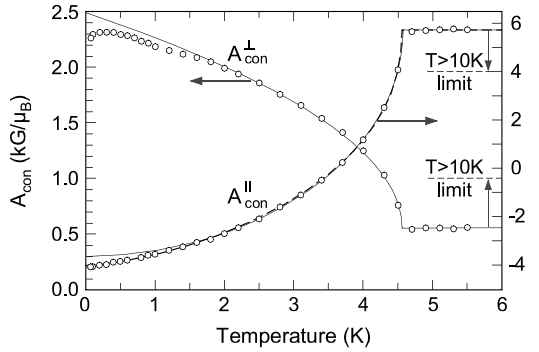

FIG. 3. Temperature dependence of the extracted contact coupling constants $A_{con}^{\perp}$ and $A_{con}^{\parallel}$ for $H_{ext} = 2.5$ T. The thin solid lines represent fits of Eq. (5) in the temperature range 1.8 K $- T_Q$ with $\gamma^{\perp} = 1$, $\gamma^{\parallel} = 2$, and $\beta = 0.5$. The heavy dashed line represents a fit in the full temperature range, allowing all parameters to vary, yielding $\beta^{\parallel} = 0.44(1)$ and $\gamma^{\parallel} = 1.51(1)$. The behavior of $A_{con}^{\perp}$ below 0.5 K is not understood.

Most of the observed strange field dependence has thus disappeared when the results are plotted versus the reduced temperature T/T_Q. The residual field dependence seen in Fig. 4 originates mainly from the amplitude $A_{con,i}(0)$, showing a shallow maximum around 1–2 kOe. Note that the unusual temperature and magnetic field dependence of the ^{11}B-NMR splitting in phase II [3] was attributed to the

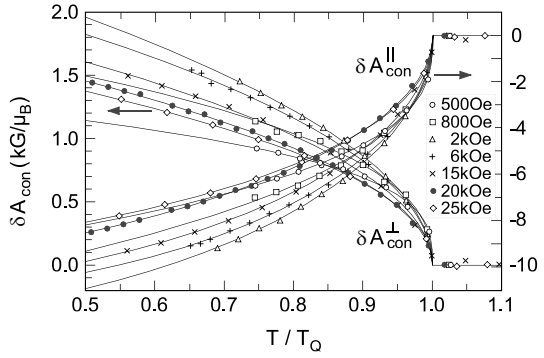

FIG. 4. Plot of $\delta A_{con}^{\perp,\parallel} = A_{con}^{\perp,\parallel}(T) - A_{con}^{\perp,\parallel}(T_Q)$ versus T/T_Q. The solid lines represent fits of Eq. (5) as described in the text. For clarity the 1 and 4 kOe data are not included in this plot.

TABLE I. List of fitted $\beta^{\perp,\parallel}$, $A_{\rm con}^{\perp,\parallel}(0)$, and $T_Q^{\perp,\parallel}$ [Eq. (5)].

$H_{\rm ext}$ (Oe)	γ, β	$A_{\rm con}^{\perp}$ (kG/μ_B)	$T_Q^{\perp}$ (K)	$A_{\rm con}^{\parallel}$ (kG/μ_B)	$T_Q^{\parallel}$ (K)
500	[a]	1.42(2)	3.21(1)	−10.40(4)	3.22(1)
800	[b]	1.96(2)	3.22(1)	−12.28(3)	3.23(1)
1k	[c]	2.74(2)	3.314(5)	−12.85(3)	3.315(5)
2k	[c]	2.75(5)	3.32(1)	−12.65(1)	3.33(1)
4k	[c]	2.626(5)	3.434(5)	−12.10(1)	3.45(1)
6k	[c]	2.591(5)	3.52(1)	−11.96(1)	3.53(1)
15k	[c]	2.26(1)	4.07(1)	−10.77(1)	4.064(5)
20k	[c]	2.054(4)	4.32(1)	−9.95(1)	4.33(1)
25k[d]	[c]	1.946(5)	4.56(1)	−9.32(1)	4.57(1)

[a] $\gamma^{\perp} = \gamma^{\parallel} \equiv 1$, $\beta^{\perp} = 0.314(7)$, $\beta^{\parallel} = 0.344(1)$.
[b] $\gamma^{\perp} = \gamma^{\parallel} \equiv 1$, $\beta^{\perp} = 0.394(5)$, $\beta^{\parallel} = 0.396(2)$.
[c] $\gamma^{\perp} \equiv 1$, $\gamma \equiv 2$, $\beta \equiv 0.5$.
[d] Fit range 1.8 K $\leq T \leq T_Q$.

field induced $\boldsymbol{m}_{\rm AFM}$ [8] and hence cannot be related to the behavior of the μ^+ Knight shift.

However, $\delta A_{\rm con}^{\perp}(T)$ shows a striking resemblance with the quadrupolar order parameter $p(T)$, Eq. (1), and suggests that $\delta A_{\rm con} \propto p = \langle O_{xy} \rangle$. In fact, the only significant intrinsic temperature dependence below T_Q, as far as we know, is carried by the quadrupolar order parameter, and hence we conclude that indeed $\delta A_{\rm con}$ reflects directly the quadrupolar order parameter. How is this possible? As already proposed in the case of UPd_3 [20] and CeAg [21], we think this is evidence that the RKKY induced conduction electron spin polarization depends on the orientation of the aspherical f-electron charge distribution (characterized by its associated quadrupole and, perhaps, hexadecapole moments) relative to the μ^+ position and its more or less spherical screening cloud of conduction electrons. Theoretical considerations support this conjecture [22]. The onset of the temperature and field dependence of $A_{{\rm con},i}$ already below 10 K, i.e., above T_Q, could point to a precursor phenomenon [23]. Note that $A_{\rm con}$ remains anisotropic, although temperature independent, for $T > 10$ K. This feature could point to a field induced (perhaps ferro) quadrupolar order, as proposed for CeAg [21,22]. The slight field dependence of $A_{{\rm con},i}(0)$ may have different origins. One possibility is that the field induced octupole moments affect the AFQ order.

The exponent β in Eq. (1) is predicted by a mean field calculation to be 0.5 [24], as found here for $H_{\rm ext} \geq 1$ kOe. The average $\beta \simeq 0.33$ extracted from the 500 Oe data, on the other hand, agrees with the value derived from the zero field nonresonant x-ray scattering intensity [11]. From resonant x-ray scattering Nakao *et al.* [9] find $\beta \simeq 0.37$ independent of $H_{\rm ext}$. Very puzzling is the 1:2 anisotropy of γ for $H_{\rm ext} \geq 1$ kOe. It implies that the order parameter viewed along and perpendicular to $\boldsymbol{r}_{{\rm Ce}-\mu^+}$ follows a different temperature dependence, a feature not understood at present. Collective excitations of the ordered quadrupole moments, analogous to magnon excitations, may be involved.

In summary, the contact hyperfine coupling constant $A_{\rm con}$ with respect to the interstitial $3d$ sites is shown to follow the same temperature and weak field dependence as the quadrupolar order parameter in phase II. We take this as evidence that $A_{\rm con}$ is, in fact, proportional to the order parameter and attribute it to an anisotropic $4f$ moment induced RKKY mechanism, which depends on the orientation of the quadrupole moment, i.e., the nonspherical $4f$ charge distribution relative to the μ^+ position. Consistent with this interpretation is the fact that $A_{\rm con}$ becomes anisotropic.

We find it remarkable that μ^+ Knight shift measurements (a local probe technique) are able to provide the same information as x-ray scattering experiments. This needs to be exploited in future investigations.

We thank the PSI and the Laboratory for Muon Spin Spectroscopy ($S\mu S$) for providing beam time and excellently working μSR instruments.

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