

Field-Induced Magnetization Distribution and Antiferroquadrupolar Order in CeB₆

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The anisotropic Knight shift of implanted positive muons (μ^+) in CeB₆ has been studied between 2.2 and 200 K in a field of 0.6 T. The results imply that the field-induced magnetization distribution is not only found at the Ce sites but also in other regions of the unit cell (e.g., near or inside the B₆ molecule, as proposed by Saitoh *et al.* [J. Phys. Soc. Jpn. Suppl. **71**, 106–108 (2002)]). While above the antiferroquadrupolar ordering temperature $T_Q \approx 3.55$ K this additional magnetization appears to be antiparallel to the Ce moments, a drastic change is observed below T_Q , and the additional magnetization is eventually aligned parallel to the Ce moments.

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Since the early 1980s the cubic, dense Kondo compound CeB₆ has been the subject of numerous and still ongoing experimental and theoretical studies [1] owing to its peculiar phase diagram that consists of a low temperature rather complex antiferromagnetic phase with $T_N \approx 2.25$ K, called phase III, an intermediate phase II, which is believed to reflect antiferroquadrupolar order [2] and develops below $T_Q = 3.3$ K, and a paramagnetic phase above T_Q . Both T_N and T_Q depend on the magnetic field and its orientation with respect to the crystal frame. Neutron diffraction [3] and NMR studies [4] have revealed that in phase II antiferromagnetic (AF) order is induced by an applied field. According to the neutron work this order appears to be of a simple G type with propagation vector $\vec{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while the NMR results were interpreted in terms of a triple- \vec{q} structure. These long-standing seemingly inconsistent pictures have recently been reconciled [5] by considering a field-induced T_{xyz} type octupolar moment of the $4f$ electrons of Ce and its associated hyperfine field at the boron sites. The microscopic origin of this hyperfine field was proposed to arise from the anisotropic hybridization of the $2s/2p$ states of boron and the $4f$ electrons possessing an O_{xy} quadrupole moment [6]. From a more recent neutron scattering work [7] it is known that the field-induced magnetic Bragg-peak intensities below T_Q show a very peculiar temperature and field dependence. This behavior could be explained in terms of a competition between the exchange coupling of dipoles and the AF coupling of the field-induced octupole moments of the T_{xyz} type. Very recently polarized neutron diffraction measurements in phase I and phase II seem to show directly that a considerable spin polarization is induced at distinct positions inside and outside of the B₆ molecule [8]. According to [8] at 5.9 T and 1.6 K as much as 30% of the induced magnetization might be associated with these additional spin polarized spots or moments. In the present

work we will show that the very peculiar behavior of the muon Knight shift in phase I and phase II seems to confirm the presence of additional moments and, moreover, demonstrates a dramatic dependence of those on the development of the antiferroquadrupolar order below T_Q . Very preliminary work was already communicated some years ago [9].

The muon Knight-shift measurements by the muon spin rotation (μ SR) technique were performed at the Paul Scherrer Institute (PSI), using the spectrometer GPS on the π M3 beam line. The sample was a newly prepared single crystal of cylindrical shape with diameters of 6 and 12 mm length. The cylinder axis coincided with the $[1\bar{1}0]$ crystal axis around which the sample could be rotated. It is enriched in ¹¹B (99.5%), since it will also be used for neutron scattering experiments. Preliminary neutron measurements showed the sample to be of excellent quality. Since the sample is relatively large no background signal originating from μ^+ stopped outside of the sample, was visible. The applied field of $H_{\text{ext}} = 0.6$ T was determined from a measurement of the μ^+ -precession frequency in an Ag sample and was oriented perpendicular to the cylinder axis.

The collected μ SR spectra showed the presence of two precession components with an amplitude ratio of $A_1/A_2 = 2/1$ over the full temperature range covered (2.3–200 K). The temperature dependence of the precession frequencies ν_1 and ν_2 was measured for $\vec{H}_{\text{ext}} \parallel [001]$ and $\vec{H}_{\text{ext}} \parallel [110]$ from 2.3 up to 200 K. The results are displayed in Fig. 1. We note that $\nu_1([110]) = \nu_2([001])$. With decreasing temperature there is a dramatic change in the frequencies starting abruptly at T_Q . Further down, independently of the orientation all frequencies become equal at ~ 2.5 K, and their order below that temperature is reversed. However, no further splitting of the μ SR signal was seen below T_Q , in contrast to NMR results [4].

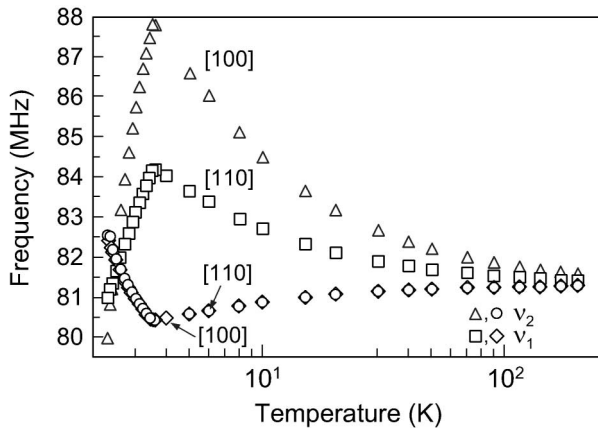


FIG. 1. Temperature dependence of ν_1 and ν_2 for $H_{\text{ext}} \parallel [001]$ and $H_{\text{ext}} \parallel [110]$.

The shift of the precession frequencies ν_i with respect to $\nu_0 = \gamma_\mu H_{\text{ext}}$ arises, as usual, from the contact hyperfine field and the dipole fields, originating from the field-induced local moments, and the demagnetization and Lorentz fields. Accordingly we can write [10]

$$\frac{\nu_i - \nu_0}{\nu_0} = \vec{b} \cdot \left[4\pi \left(\frac{1}{3} - \vec{N} \right) \cdot \vec{\chi}_b + (A_c + \vec{A}_{\text{dip}}) \cdot \vec{\chi}_{\text{loc}} \right] \cdot \vec{b}, \quad (1)$$

where $\vec{b}_i = \vec{H}_{\text{ext}}/H_{\text{ext}}$, $\vec{N} = \text{demagnetization tensor}$, A_c is the contact coupling constant (assumed to be isotropic), \vec{A}_{dip} is the dipolar coupling tensor which depends only on the μ^+ site and the induced moment sublattice, $\vec{\chi}_b$ is the bulk-susceptibility tensor in emu/cm³ (in our case $\vec{\chi}_b = \chi_b \cdot \vec{1}$), and $\vec{\chi}_{\text{loc}}$ is a local susceptibility tensor (in emu/mol) which describes the magnetic response of the magnetic ions next to the μ^+ . The second term in Eq. (1) is what is usually called the Knight shift. From a measurement of the dependence of the ν_i on the orientation of \vec{H}_{ext} in the (1 $\bar{1}$ 0) crystal plane (not shown) it is seen that the ν_i are at a maximum or minimum, respectively, if $\vec{H}_{\text{ext}} \parallel [001]$ or $\vec{H}_{\text{ext}} \parallel [110]$. This implies that \vec{A}_{dip} contains only diagonal elements. Interstitial sites with this property are the $c\{(\frac{1}{2}, \frac{1}{2}, 0)$ and equivalent $\}$ and $d\{(0, 0, \frac{1}{2})$ and equivalent $\}$ sites, independent of whether the Ce or the B sublattice carry the induced moments. An inspection of the CeB₆ crystal structure (see Fig. 2) shows that these are the only likely interstitial sites. However, the distance between a c site and a boron atom is only 0.83 Å, which appears too small to allow the μ^+ to occupy it. Hence it seems that the d site in all likelihood is the only possible μ^+ site. Table I collects calculated A_{ii}^{dip} for the d site assuming different sublattices for the induced moments. For the sake of simplicity in the following we assume the moments to be pointlike. The Knight-shift term in Eq. (1) for \vec{H}_{ext} confined to the (1 $\bar{1}$ 0) plane may now be

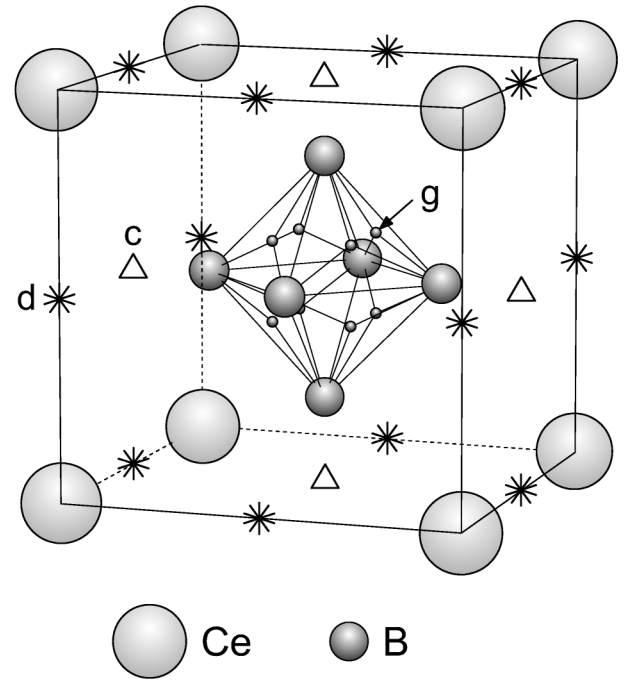


FIG. 2. Crystal structure of CeB₆. Indicated are the d , c , and g sites. The boron atoms occupy the f sites; the b site (not marked) is at the center of the cube. The μ^+ is located at the d site. For clarity the c site at the front and back face are not shown.

expressed as follows for the different d sites, using only the A_{zz}^{dip} component for the $(0, 0, \frac{1}{2})$ site:

$$\begin{aligned} K\left(0, 0, \frac{1}{2}\right) &= [A_c + A_{zz}^{\text{dip}} P_2^0(\cos\theta)] \chi_{\text{loc}} = K_2, \\ K\left(0, \frac{1}{2}, 0\right) &= \left[A_c - \frac{1}{2} A_{zz}^{\text{dip}} P_2^0(\cos\theta) \right] \chi_{\text{loc}} = K_1, \\ K\left(\frac{1}{2}, 0, 0\right) &= \left[A_c - \frac{1}{2} A_{zz}^{\text{dip}} P_2^0(\cos\theta) \right] \chi_{\text{loc}} = K_1. \end{aligned} \quad (2)$$

(θ is the angle between \vec{H}_{ext} and the [001] axis.) Hence the appearance of a split signal with amplitude ratio 1:2

TABLE I. Collection of A_{ii}^{dip} (kG/ μ_B) with respect to the d site $(0, 0, \frac{1}{2})$, assuming different sublattices for the induced moments. For all cases $A_{i \neq j}^{\text{dip}} = 0$. The A_{ii}^{dip} for the two other d sites $(0, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 0, 0)$ are obtained by cyclic permutation of the quoted A_{ii}^{dip} , e.g., $A_{zz}^{\text{dip}}(0, \frac{1}{2}, 0) = A_{zz}^{\text{dip}}(\frac{1}{2}, 0, 0) = -1/2 A_{zz}^{\text{dip}}(0, 0, \frac{1}{2})$.

$A_{xx} = A_{yy}$	A_{zz}	$A_{xx} = A_{yy}$	A_{zz}
Ce-(a -site) sublattice		B-(f -site) sublattice	
-1.97	3.94	3.65	-7.30
b -site sublattice		c -site sublattice	
0.57	-1.14	1.97	-3.94
g -site sublattice			
4.52	-9.04		

and anisotropy ratio 2:1 is consistent with a d site assignment of the μ^+ . Further, the observation that $\nu_2([110]) = \nu_1([001])$ implies that χ_{loc} and A_c are indeed isotropic. The next step is to determine the constant A_{zz}^{dip} .

In order to circumvent the problem of correcting for the demagnetization and Lorentz field we calculate

$$\Delta K_1 = \frac{1}{\nu_0} [\nu_1([001]) - \nu_1([110])] = -\frac{3}{4} A_{zz}^{\text{dip}} \chi, \quad (3a)$$

$$\Delta K_2 = \frac{1}{\nu_0} [\nu_2([001]) - \nu_2([110])] = +\frac{3}{2} A_{zz}^{\text{dip}} \chi, \quad (3b)$$

(remember that the sample was rotated around in cylinder axis and therefore the demagnetization factor was constant) and plot it versus χ_b (Clogston-Jaccarino plot). We find (see Fig. 3) that the K_i scale linearly with χ_b from just above T_Q to 200 K, the maximum temperature used. The slopes have the ratio $-\frac{1}{2}$, as required, and we find $A_{zz}^{\text{dip}}(0, 0, \frac{1}{2}) = 1.59 \frac{\text{mol}}{\text{emu}} = 5.93 \frac{\text{kG}}{\mu_B} (\pm 0.2\%)$. Comparing this value with the entry in Table I for the Ce sublattice, it is obviously too large. [For a c site assignment ($A_{zz}^{\text{dip}} = -1.14 \text{ kG}/\mu_B$) the discrepancy would be even more serious.] *This is the key observation.* One reason that it comes out too large may be that the local atomic susceptibility of the Ce ions is larger by 50% than the bulk susceptibility, but displays the same temperature dependence. It does not seem likely that this is a muon induced effect, given the unchanged temperature dependence. Hence excluding a muon induced origin, there must be other negative moment densities which bring down the total susceptibility to the bulk values. If there are other regions with induced magnetization well separated from the μ^+ sites, they will be the source of additional dipole fields (and also contact fields) at the μ^+ sites. In this case Eq. (3a) [and correspondingly Eq. (3b)] should be replaced by

$$\Delta K_1 = -\frac{3}{4} [A_{zz}^{\text{dip}}(\text{Ce})\chi_{\text{Ce}} + A_{zz}^{\text{dip}}(\text{ad})\chi_{\text{ad}}], \quad (4)$$

where $A_{zz}^{\text{dip}}(\text{ad})$ is the dipolar coupling constant associated with the new source, χ_{ad} is the associated additional susceptibility, and for the bulk susceptibility

$$\chi_b = \chi_{\text{Ce}} + \chi_{\text{ad}} = (1 + \alpha)\chi_{\text{Ce}}, \quad (5)$$

since the linear dependence of K_1 and K_2 on χ_b above T_Q implies that χ_{Ce} and χ_{ad} exhibit the same functional form for the temperature dependence. Then

$$\Delta K_1 = -\frac{3}{4} [A_{zz}^{\text{dip}}(\text{Ce}) + \alpha A_{zz}^{\text{dip}}(\text{ad})] \frac{1}{1 + \alpha} \chi_b, \quad (6)$$

and the effective dipolar coupling constant is given by

$$A_{zz}^{\text{dip}} = \frac{1}{1 + \alpha} [A_{zz}^{\text{dip}}(\text{Ce}) + \alpha A_{zz}^{\text{dip}}(\text{ad})]. \quad (7)$$

From Table I we see that positive moments at a variety of other sites are all associated with negative $A_{zz}^{\text{dip}}(\text{ad})$ and hence, if present, would reduce the effective A_{zz}^{dip} . Negative induced moments, however, would

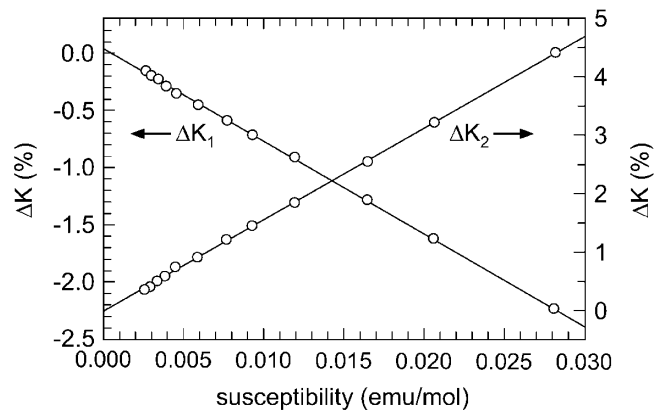


FIG. 3. Plot of ΔK_1 and ΔK_2 versus the bulk susceptibility χ_b for $T > T_Q$ (Clogston-Jaccarino plot).

enhance the effective A_{zz}^{dip} . Therefore an enlarged susceptibility of the Ce ions and the appearance of negatively polarized spin densities on the f -, b -, c -, or g -site sublattices would combine to push the effective A_{zz}^{dip} to larger values. E.g., with $A_{zz}^{\text{dip}} = 5.93 \text{ kG}/\mu_B$, $A_{zz}^{\text{dip}}(\text{Ce}) = 3.94 \text{ kG}/\mu_B$, and $A_{zz}^{\text{dip}}(\text{ad})$ taken from Table I we arrive at $\alpha(\text{f site}) = -0.14$, $\alpha(\text{c site}) = -0.20$, $\alpha(\text{g site}) = -0.13$, and $\alpha(\text{b site}) = -0.28$. These values imply that the induced negative magnetization at a variety of sites inside and outside of the B_6 molecule amounts to 13%–28% of the (positive) magnetization associated with the Ce ions. It is interesting to note that the calculation in [6], which considers the anisotropic hybridization of the boron $2s$ and $2p$ electrons with the $4f$ electrons, predicts an induced negative moment density on the B_6 molecule which would be in qualitative agreement with our present findings.

We now turn to the behavior of the anisotropic Knight shift below T_Q . Figure 4 shows ΔK_1 and ΔK_2 as a function of temperature. As in Fig. 1, a dramatic change appears at T_Q and both ΔK_1 and ΔK_2 pass through zero at ~ 2.5 K. Except for temperatures close to 2.5 K $\Delta K_1/\Delta K_2$ remains close to $-1/2$, proving the dipolar origin of the Knight-shift anisotropy. Equation (4) then implies that the two terms in this equation must cancel each other at ~ 2.5 K. In view of the fact that $A_{zz}^{\text{dip}}(\text{Ce})$ is a given parameter (excluding the possibility of a μ^+ site change) and that the bulk susceptibility χ_b grows even faster below T_Q with decreasing temperature [11] (see Fig. 4a) it is obvious that the second term in Eq. (4) must first shrink and then change sign as T decreases below T_Q . This implies that the susceptibility χ_{ad} must become strongly temperature dependent [since the $A_{zz}^{\text{dip}}(\text{ad})$ are as well temperature independent] and must change from negative to positive somewhere below T_Q . This is in fact consistent with the behavior of χ_b below T_Q [see Eq. (5)].

Obviously the onset of the antiferroquadrupolar order coincides with the change of behavior of χ_{ad} (or χ_b), implying that the induced magnetization away from the

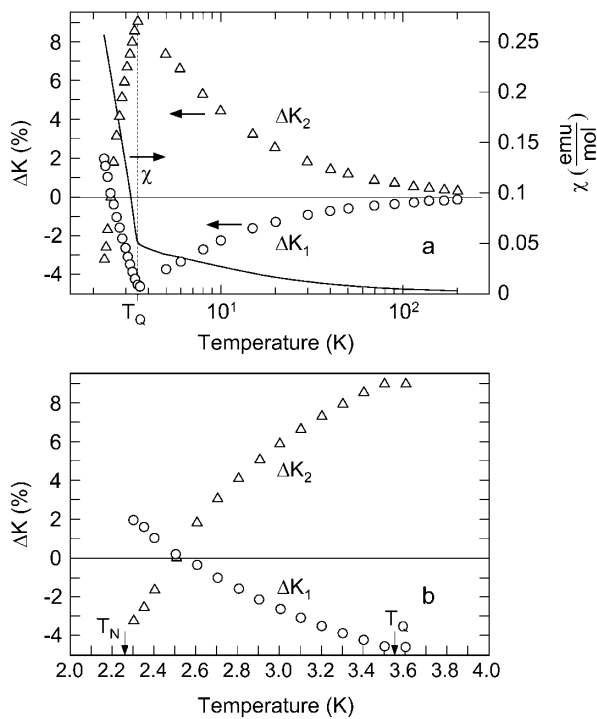


FIG. 4. Temperature dependence of ΔK_1 , ΔK_2 and of the bulk susceptibility χ_b [11]: (a) full temperature range; (b) blowup of the low-temperature region.

Ce ions is closely connected to the quadrupolar order. Following [6] this may be explained by the anisotropic hybridization of the Ce $4f$ electrons with the boron $2s$ and $2p$ electrons, which depends on the relative orientation of the nonspherical $4f$ -charge distribution and the $2s$ and $2p$ distributions.

Not surprisingly, the onset of the quadrupolar order is also reflected in the isotropic contact hyperfine contribution to the Knight shift: $\langle K_i \rangle = \frac{1}{3}K_i([001]) + \frac{2}{3}K_i([110])$. Like for the dipolar part, the $\langle K_i \rangle$ show a sharp break in behavior at T_Q , similar in appearance to that in Figs. 1 and 4. Since the contact hyperfine field reflects the spin polarization of the conduction electrons at the μ^+ , this spin polarization is obviously not only affected via the RKKY mechanism by the moments induced on the Ce sites but also by the induced moment density elsewhere. It also seems that the induced spin density at the μ^+ sites is inhomogeneously distributed below T_Q as may be inferred from a pronounced increase of the relaxation rates of the precession signals below T_Q (not shown). A similar behavior has recently been seen in UPd₃ in the ordered quadrupolar phase and has been attributed to an anisotropic RKKY mechanism in the presence of quadrupolar order [12].

As mentioned above, below T_Q no further splitting of the μ SR signal is observed in contrast to NMR results [4]. This is indeed to be expected if the induced AF order,

assumed to involve the Ce sublattice, is of the simple G type. In this case the dipolar and contact hyperfine fields will cancel at the μ^+ site, but not at the boron sites. It appears that both the induced AF order (on the Ce sites) and the induced magnetization density around the B₆ molecule involve the field-induced T_{xyz} type of octupole moment in the antiferroquadrupolar ordered state. However, also above T_Q the field induced magnetization density around the B₆ molecule is present (although with a different behavior) while the field-induced AF order is restricted to temperatures below T_Q and therefore intimately connected to the antiferroquadrupolar order.

In summary, the present μ SR results reveal that field-induced moments do not only appear at the Ce sites but also in other regions around or inside the B₆ molecule in qualitative agreement with theoretical prediction [6] and recent neutron scattering results [8], and that this phenomenon is strongly affected by the onset of the antiferroquadrupolar order. It is tempting to consider that in phase III, below T_N , these additional moments are present as well, induced by the ordered Ce moments, and that their presence may resolve the long-standing problem that the eight observed spontaneous μ^+ precession frequencies below T_N [13] are not reproducible by the magnetic structure proposed on the basis of the neutron diffraction work [3].

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