Unveiling the 4f electrons hybridization in the $CeCuSb_2$ heavy fermion

Davi Zau[1*], G. S. Freitas[1] P. G. Pagliuso[1] and R. R. Urbano[1]

1 "Gleb Wataghin" Institute of Physics, University of Campinas - UNICAMP, Campinas, São Paulo 13083-859, Brazil
* davizau@ifi.unicamp.br

August 15, 2022

International Conference on Strongly Correlated Electron Systems (SCES 2022)
Amsterdam, 24-29 July 2022
doi:10.21468/SciPostPhysProc.?

Abstract

In this work, we performed systematic Nuclear Magnetic Ressonance (NMR) and magnetic susceptibility experiments in $CeCuSb_2$ singlecrystals. We obtained the NMR spectra and the transferred hyperfine coupling for the ^{63}Cu site aiming to observe the correlation between the hyperfine coupling and the crystal eletric field (CEF) effects. Besides, we tried to elucidate the magnetic structure through NMR measurements at different magnetic fields alignments. We observed a magnetic transition at $T \approx 8K$ much higher than the Neel temperature T_N measured by magnetization suggesting the developing of short range magnetic order at this temperature. Also, the wipe out of the main resonance line and a persistent spin-echo signal through all the frequency swept range further support an incomensurate magnetic structure. Furthermore, the small values found for the transferred hyperfine coupling constant suggest a scenario much more localized than that observed for the $CeTIn_5$ (T = Co,Rh,Ir). Additionally, a drastic change in the hybridization of the ^{63}Cu site with the $4f^1$ Ce^{3+} electrons in distinct magnetic field orientation leads to a possible mapping of the 4f CEF ground-state orbital via NMR measurements.

Contents

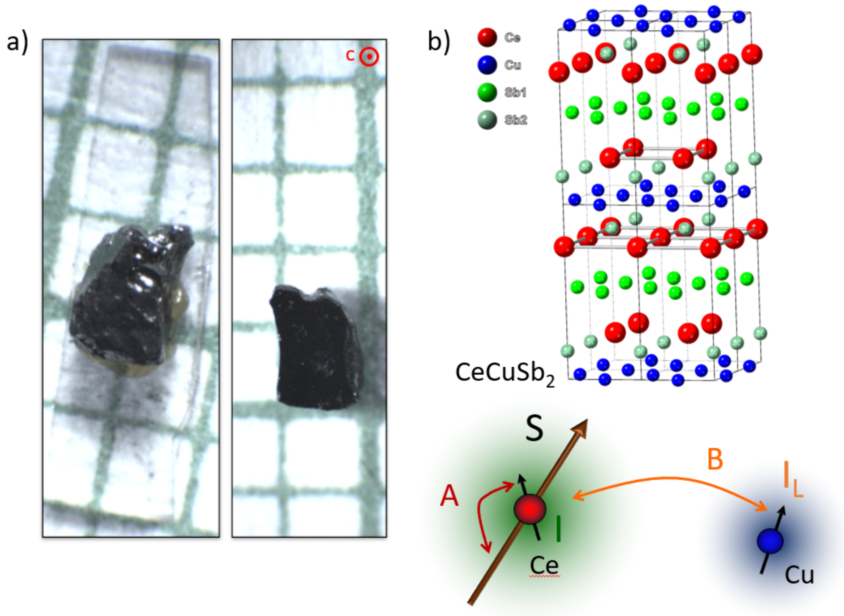

Figure 1: a) $CeCuSb_2$ sample used in the study. b) $CeCuSb_2$ structure with a scheme of the transferred hyperfine coupling B_{hf} below.

1 Introduction

In recent years, scientists put much effort into understanding unconventional superconductivity [1,2] and several new families of possible superconductors were found [3,4]. One of them is the heavy fermions superconductors. They had shown promising underlying physical properties, mainly due to the interplay of the Ruderman-Kittel-Kasuya-Yosida (RKKY) and Kondo interactions [5], which leads to a plethora of complex quantum condensed matter phenomena beyond superconductivity. Properties like field-induced and quantum phase transitions, coexistence of magnetism and superconductivity, and many others are not uncommon in such systems [6,7]. However, a lower energy scale often despised that showed to play an important role in the definition of the ground-state properties of these materials is the crystalline electric field (CEF) [8]. Recently, a study exhibited a direct relation between the magnetic and superconducting transition temperatures (T_N and T_C respectively) with the CEF effects for the Ce-115 family [9]. Moreover, a recent essay established a connection between the CEF and the transferred hyperfine coupling for the same compounds, through nuclear magnetic resonance (NMR) [10].

To observe whether the connection holds for other heavy fermion compounds such as $CeCu(Bi,Sb)_2$, we performed systematic NMR for the ^{63}Cu sites ($I = \frac{3}{2}$, $\gamma_N = 11.285\,\frac{MHz}{T}$) and magnetic susceptibility measurements in $CeCuSb_2$ single crystals. Through the Knight shift data, we directly extracted the transferred hyperfine coupling B_{hf} via the Clogston-Jaccarino plot [11]. Moreover, within a mean-field framework, we obtained the CEF parameters from magnetic susceptibility fittings [12]. Finally, with previous results reported for the $CeCuBi_2$ sample [13], we could evaluate the correlation between the CEF parameter and the hyperfine coupling in this family.

In addition, we have also attempted to elucidate the $CeCuSb_2$ magnetic structure anisotropy through NMR measurements, mainly in two field directions: perpendicular and parallel to the crystallographic c axis. Employing careful analysis of the Knight shift in both directions, we obtained some hint about the orientation as well as the commensurability of the magnetic structure.

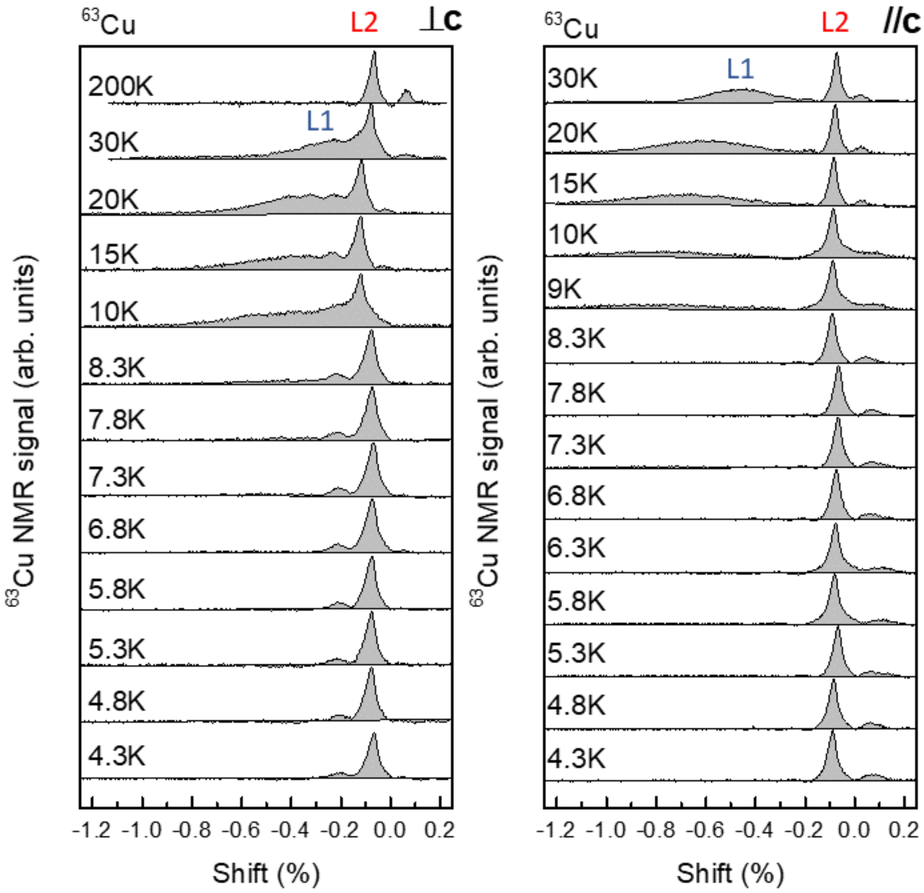

Figure 2: ^{63}Cu NMR spectra in two magnetic field orientations parallel and perpendicular to the c axis at different temperatures. The resonance lines L1 and L2 were indexed as shown.

2 Methods

$CeCuSb_2$ single crystals (Fig 1.a) were obtained via the flux-growth method and the crystallographic structure was verified and reported in [14]. We carried out the magnetic susceptibility measurements using a commercial Superconductor Quantum Interferometer Device (SQUID) at $7\,T$.

We performed the NMR measurements using a high homogeneity superconducting magnet with a variable $12.1\,T$ field in a Helium-4 cryostat. The rf coil was manufactured with silver wire and set to be swept within the resonance frequency between $70\,MHz > \nu > 80\,MHz$. The frequency-swept ^{63}Cu NMR spectrum were obtained by stepwise summing the Fourier transform of the spin-echo signal.

3 Results and Discussion

The NMR spectra as function of temperature in both field orientations (perpendicular and parallel to the crystallographic c axis) are shown in Figure 2. One can observe some striking features: There are mainly 2 resonance lines indexed as Figure 2. The broader line disappears

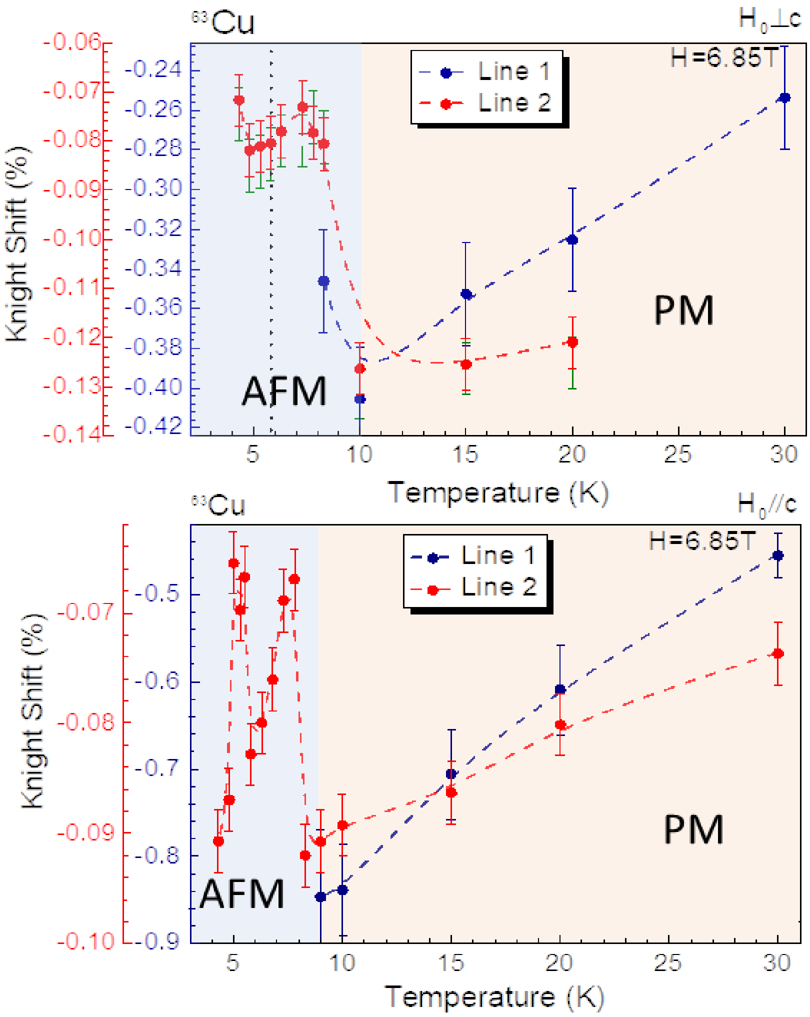

Figure 3: Knight shift as function of temperature for both field orientations. We can see a clear change in behavior right below $\approx 10\,K$ due to the onset of the magnetic transition.

at low temperatures where the onset of the magnetic order kicks in leading us to assign it as the main resonance line in $CeCuSb_2$. The other resonance is narrower and was attributed to ^{63}Cu sites near intermetallic vacancies in the crystal due to its small shift.

We extracted the Knight shift shown in Figure 3 through best Gaussian fits of each peak. It is clear that all resonances probes the onset of an antiferromagnetic transition near $T = 8\,K$. This is unexpecting since the magnetic susceptibility measurements showed a $T_N = 5.8\,K$ indicating that some short-range magnetic order settles down before the long-range antiferromagnetic ordering. Furthermore, although unclear in Fig.2, we observed a persistent spin-echo signal in the whole measured frequency range below $8\,K$, which suggests a possible incommensurate magnetic structure for $CeCuSb_2$. Additionally, as mentioned above, the main ^{63}Cu NMR resonance signal disappears below the transition temperature, avoiding us to do a precise determination of the magnetic structure of our sample. This complex magnetic structure could also explain the supression of T_N when compared with that of $CeCuBi_2$ [13], since it could lead to a more unstable magnetic ordering able to settle down only at lower temperatures. This corroborates with the rising magnetic frustration illustrated by the increase of the magnetic frustration parameter ($\frac{|\theta_{CW}|}{T_N}$) found in Ref [14].

We also measured the magnetic susceptibility at the same magnetic field used in the NMR measurements in order to obtain the hyperfine coupling constant. This can be accomplished through the Clogston-Jaccarino plot of the Knight shift as function of the susceptibility shown in Figure 4. Thus, from the slope of the data one may directly extract the hyperfine coupling

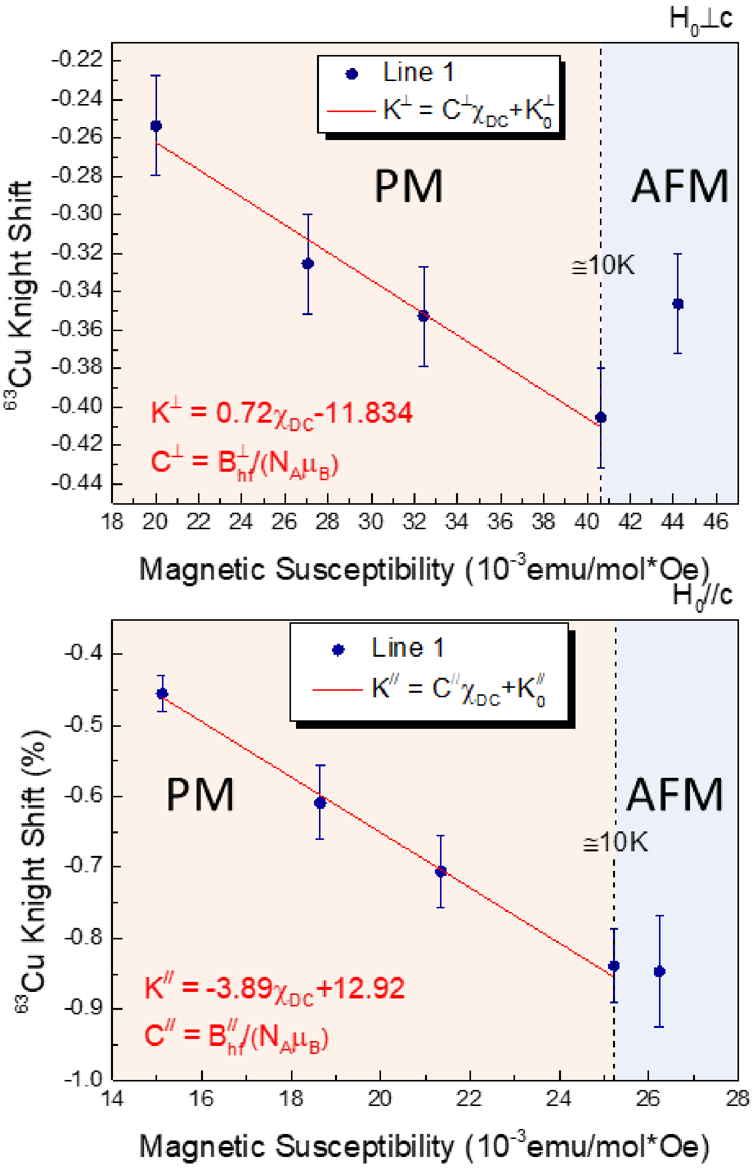

Figure 4: Clogston-Jacarinno plots for both field orientations, $H_0 \perp c$ and $H_0 \parallel c$. The temperature is an implicit parameter. A clear linear behavior is observed for $T \gtrsim 10\,K$ (PM phase).

constant B for both field orientations for $CeCuSb_2$. In Table 1, we present the hyperfine coupling constants for each resonance observed in $CeCuSb_2$ and the CEF parameter α from the literature [13, 14], which characterizes the degree of mixing between the J_z manifolds and is directly related to the spatial anisotropy of the 4f CEF orbital as detailed in Ref [10], in other words, its the spin $S = 5/2$ contribution to the ground state wavefunction of the $4f^1$ Ce^{3+} electrons as illustrated at Fig. 5. The results for B_{hf} of $CeCuBi_2$ are also presented [13]. The CEF ground state scheme for $CeCuBi_2$ and $CeCuSb_2$ is shown in Figure 5. However, although we see a drastic change in the CEF parameters, there is no significant change in the ^{63}Cu hy-

Table 1: Transfered hyperfine coupling constants and $|\pm 5/2\rangle$ spin ground state contribution (α) as illustrated in Fig 5. Here, $B^{\parallel}$ ($B^{\perp}$) stands for the measurements done with the external field $H_0 \parallel c$ ($H_0 \perp c$). One can see a drastic change in the 4f CEF parameter α but this change is not probed by the hyperfine coupling for $H_0 \perp c$. In the other magnetic field orientation, the missing value for $CeCuBi_2$ is due to the metamagnetic transition near 6 T.

	L1	L2	$CeCuBi_2$
α	0.43	0.43	0.98
$B^{\parallel}(kOe/\mu_B)$	2.1(1)	0.08(1)	-
$B^{\perp}(kOe/\mu_B)$	0.4(1)	0.02(1)	0.7(1)

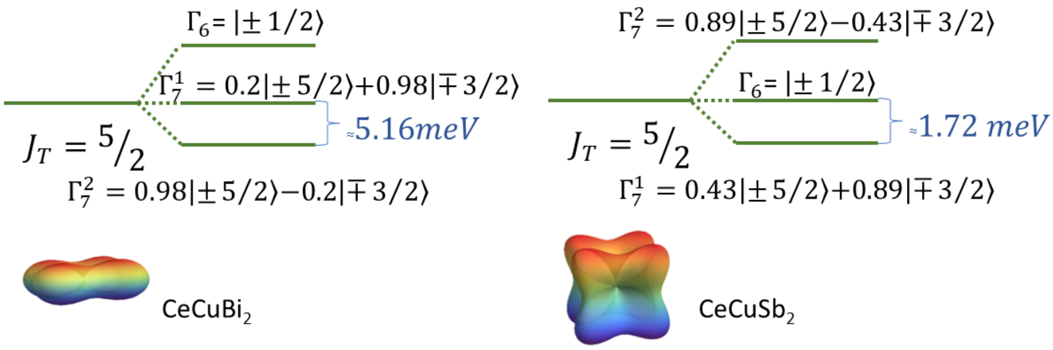

Figure 5: Scheme of the CEF ground state for the $4f^1$ Ce^{3+} electrons for $CeCu(Bi,Sb)_2$ with the respective orbital shown below. Here, α is defined as the $|5/2\rangle$ contribution to the ground-state.

bridization when the field is applied in the ab plane. Besides, if one compares the hyperfine coupling results with the values obtained for the Ce-115 compounds, one realizes a rather reduced energy scale indicating a lower ^{63}Cu hybridization with the Ce^{3+} $4f^1$ electrons. However, a clear increase in the hyperfine coupling for the main resonance line is noticed when comparing the results in different the magnetic field orientation. This increase is related to a larger $|\mp 3/2\rangle$ character of the Ce^{3+} 4f CEF ground state wave function in $CeCuSb_2$ compared to that in $CeCuBi_2$, since the Cu-site is off the Ce plane. Therefore, this might indicate that NMR is able to map the orientation of the 4f CEF orbital in the structure, as shown in the scheme of Fig 6. Nonetheless, to confirm this claim for the $CeCuBi_2$ sample, a complete set of field orientations to map the ground state orbital is required.

4 Conclusion

In conclusion, our study pointed out the possibility of an incommensurate magnetic structure for $CeCuSb_2$ due to the sudden wipe out of the ^{63}Cu resonance line 1 and the higher T_N observed. Also, we were able to probe the $4f^1$ CEF ground-state orbital for this sample. The low values of hyperfine coupling for both samples indicates a quite localized scenario if compared with the members of the Ce-115 family. However, we observed a drastic change in the hyperfine coupling constant as function of magnetic field alignment, which might be related to the actual spacial orientation of the $4f^1$ CEF orbital in the crystal structure. Furthermore, NMR is suggested as a suitable technique ideal to map the CEF ground state in heavy fermion structures..

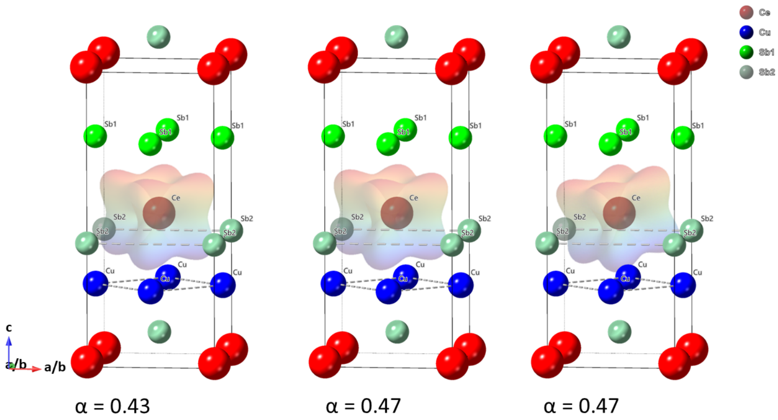

Figure 6: Illustration of the $4f^1$ CEF ground-state orbital for slightly different values of α and orientation in the $CeCuSb_2$ structure. One can see that a change in the orbital alignment would drastically change the ^{63}Cu site hybridization with the Ce^{3+} $4f^1$ electrons probed by the hyperfine coupling constant.

Figure 7: Logo

Acknowledgements

This work was performed under the auspices of the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Grant # 88887.352079/2019-00, by the Conselho Nacional de Pesquisa e Desenvolvimento Tecnológico (CNPQ) – (Grants 304496/2017-0, 309483/2018-2, 314587/2021-7, 161490/2021-2) and by the Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP) (Grants number: 2012/05903-6, 2016/14436-3, 2017/10581-1, 2018/11364-7, 2019/26247-9)

References

[1] S. Seo, X. Lu, J. Zhu, R. Urbano, N. Curro, E. Bauer, V. Sidorov, L. Pham, T. Park, Z. Fisk *et al.*, *Disorder in quantum critical superconductors*, Nature Physics **10**(2), 120 (2014).

[2] B.-L. Young, R. Urbano, N. Curro, J. Thompson, J. Sarrao, A. Vorontsov and M. Graf, *Microscopic evidence for field-induced magnetism in cecoin 5*, Physical review letters **98**(3), 036402 (2007).

[3] C. Petrovic, P. Pagliuso, M. Hundley, R. Movshovich, J. Sarrao, J. Thompson, Z. Fisk and P. Monthoux, *Heavy-fermion superconductivity in cecoin5 at 2.3 k*, Journal of Physics: Condensed Matter **13**(17), L337 (2001).

[4] D. Aoki, A. Nakamura, F. Honda, D. Li, Y. Homma, Y. Shimizu, Y. J. Sato, G. Knebel, J.-P. Brison, A. Pourret *et al.*, *Unconventional superconductivity in heavy fermion ute2*, journal of the physical society of japan **88**(4), 043702 (2019).

[5] P. Coleman, *Heavy fermions and the kondo lattice: a 21st century perspective*, arXiv preprint arXiv:1509.05769 (2015).

[6] R. Urbano, B.-L. Young, N. Curro, J. Thompson, L. Pham and Z. Fisk, *Interacting antiferromagnetic droplets in quantum critical cecoin 5*, Physical review letters **99**(14), 146402 (2007).

[7] Y.-f. Yang, R. Urbano, N. J. Curro, D. Pines and E. Bauer, *Magnetic excitations in the kondo liquid: Superconductivity and hidden magnetic quantum critical fluctuations*, Physical review letters **103**(19), 197004 (2009).

[8] C. Adriano, P. Rosa, C. Jesus, T. Grant, Z. Fisk, D. J. Garcia and P. Pagliuso, *Magnetic properties of nearly stoichiometric ceaubi2 heavy fermion compound*, Journal of Applied Physics **117**(17), 17C103 (2015).

[9] T. Willers, F. Strigari, Z. Hu, V. Sessi, N. B. Brookes, E. D. Bauer, J. L. Sarrao, J. Thompson, A. Tanaka, S. Wirth *et al.*, *Correlation between ground state and orbital anisotropy in heavy fermion materials*, Proceedings of the National Academy of Sciences **112**(8), 2384 (2015).

[10] P. Menegasso, J. Souza, I. Vinograd, Z. Wang, S. Edwards, P. Pagliuso, N. Curro and R. Urbano, *Hyperfine couplings as a probe of orbital anisotropy in heavy-fermion materials*, Physical Review B **104**(3), 035154 (2021).

[11] A. Clogston, V. Jaccarino and Y. Yafet, *Interpretation of knight shifts and susceptibilities of transition metals: Platinum*, Physical Review **134**(3A), A650 (1964).

[12] P. Pagliuso, D. Garcia, E. Miranda, E. Granado, R. Lora Serrano, C. Giles, J. Duque, R. Urbano, C. Rettori, J. Thompson *et al.*, *Evolution of the magnetic properties and magnetic structures along the r m m in 3 m+ 2 (r= ce, nd, gd, tb; m= rh, ir; and m= 1, 2) series of intermetallic compounds*, Journal of applied physics **99**(8), 08P703 (2006).

[13] C. Adriano, P. Rosa, C. Jesus, J. Mardegan, T. Garitezi, T. Grant, Z. Fisk, D. Garcia, A. Reyes, P. Kuhns *et al.*, *Physical properties and magnetic structure of the intermetallic cecubi 2 compound*, Physical Review B **90**(23), 235120 (2014).

[14] G. Freitas, M. Piva, R. Grossi, C. Jesus, J. Souza, D. Christovam, N. Oliveira Jr, J. Leao, C. Adriano, J. W. Lynn *et al.*, *Tuning the crystalline electric field and magnetic anisotropy along the cecubi 2- x sb x series*, Physical Review B **102**(15), 155129 (2020).