

Dear Editor,

Hereby we resubmit the manuscript *Unveiling the 4f electrons hybridization in the CeCuSb₂ heavy fermion*, by Davi Zau, G.S. Freitas, P.G. Pagliuso and R. R. Urbano for your reconsideration. We are grateful to the Referee for his thorough revision and appreciation of the great effort to get and analyze such experimental data as well as with his positive evaluation of our manuscript.

In this revised version we rephrased some part of the discussion and corrected the grammar in order to comply with all necessary modifications.

In the following, we present the **Summary of Changes** together with the referee comments. We answered all questions and explained some issues not so clear in the previous version in detail.

We strongly believe that the manuscript in its revised version is both technically accurate and of sufficient significance to merit publication.

Sincerely yours,

Davi Zau on behalf of all coauthors.

Referee:

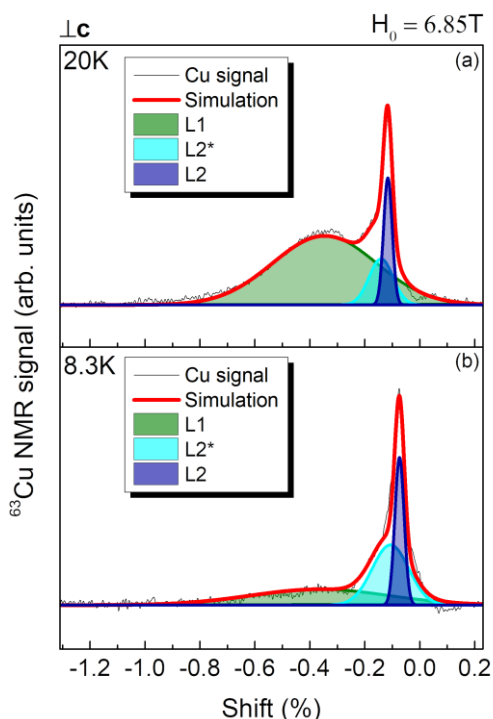
1. In Fig. 2 the main results of the paper are presented: NMR spectra. Several (broad) peaks are observed, but only L1 and L2 get labels. Not everything is clear: L1 for field perpendicular to c is broad and seems to consist of 3 subpeaks. (e.g., at 20 K). Please explain. How is its value determined? What are the peaks with a positive Knight shift. Explain this to the non-expert reader.

[Authors reply:](#)

We thank the referee for these valuable comments.

In fact, this sample is not so easy to be grown with perfect crystallization and/or orientation. So, one should expect some level of imperfections/defects/vacancies which may result in a ^{63}Cu NMR spectrum with a broad line and/or multiple peaks due to the distribution of the local environment. In fact, as reported by G. S. Freitas et al. a small amount of 14% vacancies was found in these single crystals. [1] NMR is a very sensitive local technique, so the presence of such vacancies will slightly change the neighborhood of the ^{63}Cu probe nuclei as distinct resonance lines often slightly shifted from the expected frequency/field.

However, we have reanalyzed all ^{63}Cu NMR data thoroughly to avoid any possible artifacts from the FFTsum procedure often used to acquire a broad spectrum. Indeed, we verified that the extra line pointed out by the referee was an artifact from the spectral analysis and it should not be evident when choosing the proper window for the spin-echo FFTsum procedure. This, however, does not affect the main findings and conclusions of our paper, and the main ^{63}Cu NMR lines, L1 and L2, remain displaying the same behavior as reported in the previous version of our manuscript.



Furthermore, instead of fitting the spectra, we now simulated all ^{63}Cu NMR spectra with 3 Gaussian lines (L1, L2 and L2*) by refining the former fitting parameters and get a better agreement between the analysis and experimental data. The ^{63}Cu NMR signals observed demonstrate the presence of two main local environments denoted by L1 and L2 (Cu near vacancies), as shown in the Figure 1. It is worth mentioning that the L2 and L2* lines have virtually the same behavior as function of temperature indicating similar ^{63}Cu environments. The narrower lines, weaker signal intensities and smaller knight shifts indicate that these signals correspond to the ^{63}Cu nearby the vacancies and thus, weakly coupled to the Ce atoms.

Figure 1 ^{63}Cu NMR signal with $H \parallel c$ at 20 and 8.3 K. The simulations combining 3 Gaussian lines (L1, L2 and L2*) are in good agreement with the inhomogeneous ^{63}Cu NMR spectra. The distinct signal intensities and knight shifts demonstrate two main ^{63}Cu neighborhoods.

Therefore, in Figures 2, 3, and 4, we present the reanalyzed spectra following the above-mentioned procedure and analysis as well as the obtained Knight Shift, and Clogston–Jaccarino data, respectively.

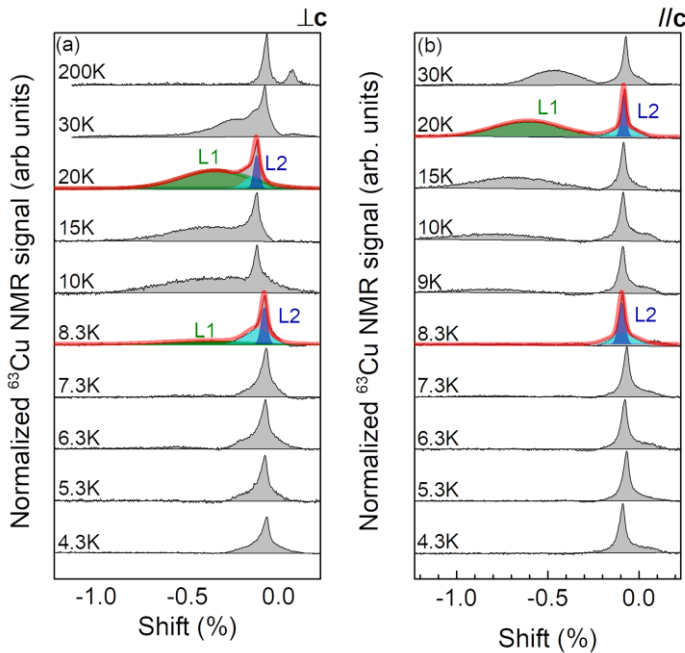


Figure 2 ^{63}Cu NMR spectra in two distinct magnetic field orientations, parallel and perpendicular to the ζc axis at different temperatures. One can see mainly two distinct resonance lines, L1 and L2, indexed as shown. L1 is much broader and disappears below $T \approx 8.3\text{K}$ and L2 is thinner and seems to be less affected with the temperature changes.

We believe that L1 is the main ^{63}Cu NMR signal in CeCuSb_2 given its significant overall behavior, i.e., greater spectral weight (intensity) and knight shift. Besides, L1 is drastically affected by the fluctuations near the transition at $T_N \sim 8.3\text{K}$ displaying the wipe out effect. On the other hand, the spectral weight of L2 and L2* compared to that of L1 at 20 K is roughly 20%. This is somewhat close to the amount of 14% of vacancies reported for our CeCuSb_2 samples [1].

Therefore, one may assume that L1 is the ^{63}Cu NMR signal coming mostly from the Cu nuclei far from vacancies and, thus, from the Cu more hybridized with the Ce atoms.

So, to obtain the Knight Shift data displayed in Figure 3, we first analyze the NMR data by fitting all resonances with 3 Gaussian lines. Then, we refined the obtained parameters (peak position, linewidth, and intensity) through a simulation process. Thus, from the best results as shown in Figure 1, we obtained the peak positions (frequencies) for each line

and calculated the Knight shift with respect to the ^{63}Cu signal (CuBr solid) from Ref. [2].

Finally, after reanalyzing all experimental data thoroughly, we observed no change in the hyperfine coupling of CeCuSb_2 for $H//c$, although a minor change was observed for $H \perp c$. The L1 line broadens drastically at low- T and near the transition due to T_2 effects, and it is difficult to obtain the Knight shift values with high precision. Besides, it is expected that a tiny change in a fitting parameter may result in different values in such a small scale. Nonetheless, we should emphasize that the anisotropy in the B_{hf} parameter is still quite significant and that the main results and conclusions remain the same as previously reported.

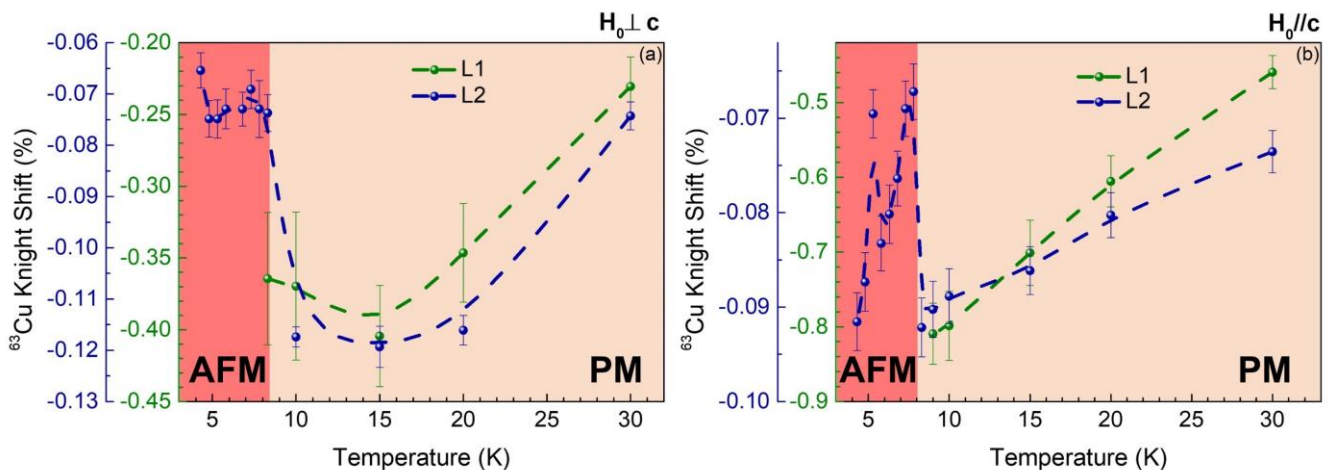


Figure 3: ^{63}Cu NMR Knight Shift data for the simulated spectra of Figure 2. One can see a clear change in the Knight shift behavior at $T < 8.3\text{K}$ for both orientations, this indicates the onset of the antiferromagnetic transition.

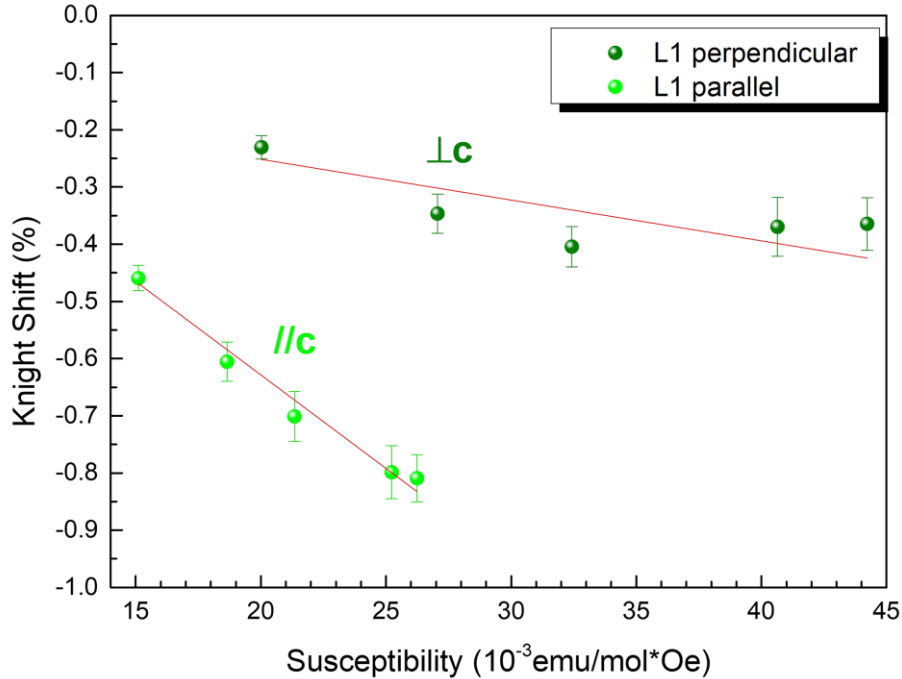


Figure 4 Clogston-Jaccarino plot for the ^{63}Cu NMR data with the magnetic field $H_0=6.85\text{T}$ applied perpendicular and parallel to the crystallographic c -axis. The points were fitted with a line following the equation $K=C\chi_{DC}+K_0$. Where $C = B_{hf}/(N_A\mu_B)$ with B_{hf} as the transferred hyperfine coupling, N_A as the Avogadro's number and μ_B as the Bohr magneton, K_0 is the contributions to the Knight shift that are independent of temperature. The results we obtained for C were $0,033(2)$ (mol Oe)/emu and $0,007(8)$ (mol Oe)/emu for the field parallel and perpendicular to the c axis respectively. One can clearly see an anisotropy in the slope of the lines.

Referee:

2. The Clogston–Jaccarino (not Jaccarino) plot is fine, from this the hyperfine coupling constant is determined. But I find the ensuing discussion about Table 1 and Fig. 5 unclear. Please be more precise.

[Authors reply:](#)

We have replaced the statement:

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 hybridization 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 $\text{Ce}^{3+} 4f$ 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 $\text{Ce}^{3+} 4f$ 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.

To:

The results for B_{hf} of CeCuBi_2 are also presented [13].

The CEF ground state scheme for CeCuBi₂ and CeCuSb₂ is shown in Figure 5. Previous results [10] suggest that the transition metal hybridization with Ce correlates well with the 4f CEF orbital shape and that a ground state wave function with larger $\pm|5/2\rangle$ than the $\pm|3/2\rangle$ contribution indicates a higher hybridization in the Cerium plane. However, although we see a drastic change in the CEF parameters for CeCuSb₂, there is no significant change in the ⁶³Cu hybridization when field is applied on the a–b plane. Besides, if one compares the hyperfine coupling values with those obtained for the Ce–115 compounds, it is easy to realize a rather reduced energy scale for the Ce–112 compounds further corroborating with a lower hybridization between ⁶³Cu and the Ce³⁺ 4f¹ electrons in this latter case.

Nonetheless, a clear increase of the hyperfine coupling is noticed for the main resonance line L1 when comparing the data with distinct magnetic field orientations. We thus claim that this hyperfine coupling enhancement might be related to a change in the magnetic moment orientation. This is supported by the shift of the easy axis from parallel to perpendicular to the crystallographic c–axis observed by magnetic susceptibility measurements in Ce–112 [14].

Therefore, this demonstrates that NMR is sensitive to such a change, and it allows us to map the configuration of the 4f CEF orbital in the structure, although a complete set of magnetic field orientations data is required to confirm this claim for the CeCuBi₂ sample. Measuring the magnetic moment orientation (magnetic structure) of these compounds and correlating that with the 4f CEF ground state orbital would bring new insight to this scenario.

Referee:

3. I also do not get the importance of Fig.6. The left 2 orbital states with $\alpha = 0.43$ and 0.47 are almost identical. Then for $\alpha = 0.47$ the most right diagram has a tilted ground state orbital. Why?

[Authors reply:](#)

We removed figure 6. The idea behind it was to elucidate how a change in the orbital shape could affect the hybridization. However, after the suggestion we agreed it was really confusing. So, we have decided to maintain a more detailed discussion.

Referee:

4. The authors should have their manuscript checked for English grammar, and correct typo's. For instance, in the abstract singlecrystals, eletric field, incomensurate. In Methods spectrum were obtained should read spectra were obtained. On the bottom of page 3: as Figure 2 should read in Figure 2. On page 4, probes should read probe, unexpecting should read unexpected. Etc.

[Authors reply:](#)

We thank the referee for pointing this out. The manuscript has been carefully revised to avoid any issue as far as English grammar, typo's and/or misspellings.

Referee:

5. Figure 7 can be deleted.

[Authors reply:](#)

Figure 7 has been deleted.

We also changed the title to best suit with the conclusions.

References:

- [1] Freitas, G.S., Piva, M.M., Grossi, R., Jesus, C.B.R., Souza, J.C., Christovam, D.S., Oliveira Jr, N.F., Leão, J.B., Adriano, C., Lynn, J.W. and Pagliuso, P.G., 2020. Tuning the crystalline electric field and magnetic anisotropy along the CeCuBi_{2-x}Sb_x series. *Physical Review B*, 102(15), p.155129.
- [2] Carter, G.C., Bennett, L.H. and Kahan, D.J., 1977. Metallic Shifts in NMR. A Review of the Theory and Comprehensive Critical Data Compilation of Metallic Materials. Part I.