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## Research article

# Electron Spin Resonance (ESR) studies on GdCuBi<sub>2</sub> intermetallic antiferromagnet

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## ABSTRACT

We report temperature dependent X-Band ( $\nu \approx 9.5$  GHz) Electron Spin Resonance (ESR) on the GdCuBi<sub>2</sub> intermetallic compound. This compound presents a metallic Curie–Weiss paramagnetic behavior at high temperatures and orders antiferromagnetically at  $T_N = 14.3$  K. Well above  $T_N$  ( $T > 250$  K), the ESR experiments revealed temperature independent  $g$ -values spectra composed of a single Dysonian Gd<sup>3+</sup> ESR line for the studied compound. Within the same temperature range, the Gd<sup>3+</sup> ESR linewidth  $\Delta H$  presents a linear broadening temperature dependence known as Korringa behavior. The obtained Korringa rate ( $\Delta H/\Delta T$ ) and  $g$ -shift ( $\Delta g$ ) from the ESR measurements, along with the study of the macroscopic properties of GdCuBi<sub>2</sub> (e.g. specific heat data and magnetic susceptibility) made it possible to explore Gd<sup>3+</sup> spin dynamics in this system based on evaluation of the exchange parameters between the Gd<sup>3+</sup> ESR probes and the conduction-electrons ( $ce$ ) in this compound. Our results indicate that the exchange bottleneck effects and a  $\mathbf{q}$ -dependent exchange interaction ( $J_{fs}(\mathbf{q})$ ) between the Gd<sup>3+</sup> and the  $ce$  are likely to be present in GdCuBi<sub>2</sub>. Disregarding the bottleneck effects in the simplest approximation, we extract the exchange parameters  $J_{fs}(\mathbf{q} = 0) \approx 380$  meV and  $\langle J_{fs}^2(\mathbf{q}) \rangle^{1/2} \approx 3.0$  meV for the Gd<sup>3+</sup> spin dynamics in GdCuBi<sub>2</sub>. These values of  $J_{fs}(\mathbf{q})$  and  $\langle J_{fs}^2(\mathbf{q}) \rangle^{1/2}$  are typical of Gd<sup>3+</sup> local moments in intermetallic materials and the small ratio  $[\langle J_{fs}^2(\mathbf{q}) \rangle / J_{fs}^2(0)] \approx 0.008$  suggests a strongly anisotropic (or quasi-2D) Fermi surface for GdCuBi<sub>2</sub>.

## 1. Introduction

Complex quantum materials include several classes of intermetallic materials containing rare-earths that commonly present an intricate interplay between crystalline electrical field (CEF) effects, Ruderman–Kittel–Kasuya–Yoshida (RKKY) magnetic coupling, and Fermi surface effects.[1] In particular, the series of intermetallic compounds  $RTX_2$  ( $R$  = Rare-earth,  $T$  = Cu and Au and  $X$  = Sb and Bi) ( $R$ -112) has been the focus of intense scientific investigation in the last decades due to the emergence of many distinct interesting physical properties such as superconductivity (SC), heavy-fermion (HF) behavior, competing anisotropic exchange interactions and CEF effects, multiple field-induced transitions, anomalous Hall effect, putative nematicity, and complex magnetic structures that were reported for this family of compounds [2–12]. Along the  $R$ -112 series, the Gd-based compounds are singular because the Gd<sup>3+</sup> ions possess an S-state ( $S = 7/2$ ,  $L = 0$ ) ground state, which makes the CEF effects become a high order effect. Thus, the Gd-based compounds can be treated as a reference compound

along a series of  $R$ -based intermetallic analogs, where the magnetic properties of the Gd-materials purely reflect important aspects of the RKKY magnetic interaction and Fermi surface effects presented in the series [11,13–20]. In addition, the Gd<sup>3+</sup> ions are suitable probes for Electron Spin Resonance (ESR) studies, which can unveil important information regarding the microscopic interaction  $J_{fs}$  between the Gd<sup>3+</sup>  $4f$  ESR probes and the conduction electrons ( $ce$ ) and the related spin dynamics of the system.

Here, we report temperature-dependent X-Band Gd<sup>3+</sup> ESR in the high- $T$  paramagnetic state of the GdCuBi<sub>2</sub> intermetallic antiferromagnetic compound. This compound presented, for  $T > 250$  K, a single Dysonian Gd<sup>3+</sup> ESR spectrum with a roughly temperature independent  $g$ -value and a Korringa thermal broadening of the Gd<sup>3+</sup> ESR  $\Delta H$ . The obtained Korringa rate ( $\Delta H/\Delta T$ ) and  $g$ -shift ( $\Delta g$ ) from the ESR experiments along with analysis of the specific heat and magnetic susceptibility data for GdCuBi<sub>2</sub>, allowed us to investigate Gd<sup>3+</sup> spin dynamics in these systems by extracting the values of the exchange parameters between the Gd<sup>3+</sup> ESR probes and the  $ce$  in these compounds.

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The extracted values for the exchange parameters and the suggested strongly anisotropic (or quasi-2D) Fermi surface for GdCuBi<sub>2</sub> can help to understand the complex anisotropic RKKY interactions commonly observed in the RCuBi<sub>2</sub> family.

## 2. Experiment

Single crystals of the GdCuBi<sub>2</sub> intermetallic system were grown using the Bi-flux method [4,5]. The crystal structure and single phase character of GdCuBi<sub>2</sub> were checked by X-ray powder diffraction. This compound crystallizes in the tetragonal *P4/nmm* structure with a stacking arrangement of GdBi-Cu-GdBi-Bi layers. Several single crystals were also submitted to elemental analysis using a commercial Energy Dispersive Spectroscopy (EDS) microprobe coupled to scanning electron microscopy. The EDS analysis revealed the stoichiometry to be close to 1:1:2 for all studied samples, namely GdCu<sub>0.95(5)</sub>Bi<sub>2</sub>. As such, along the text, when we referred to the compound GdCuBi<sub>2</sub>, we are considering the real stoichiometry of GdCu<sub>0.95(5)</sub>Bi<sub>2</sub>. Furthermore, it is important to point out that the vacancies are absence of Cu atoms and cannot be directly associated with presence of Cu<sup>2+</sup>. This defect could be spin-less or could have a free 1/2 spin (not obviously Cu<sup>2+</sup>). From the low-T ( $T < 7$  K) Curie tail in the magnetic susceptibility data in the Fig. 1, we estimated that the free 1/2 spin defects are not larger than 1%. As such, it is very unlikely that these free spins could give any contribution to the ESR of 100% of Gd ( $S = 7/2$ ) at very high temperature.

The ESR experiments were performed in a commercial bench-top ESR spectrometer equipped with a TE<sub>102</sub> cavity operated at room temperature, and temperature-dependent ESR experiments were done using a N<sub>2</sub> gas-flux temperature controller. Specific heat experiments were done using a commercial small-mass calorimeter, which employs a quasi-adiabatic thermal relaxation technique. The temperature-dependent magnetic susceptibility data were acquired using a commercial superconducting quantum interference device. The electrical resistivity experiments were done using a commercial low-frequency AC resistance bridge and samples mounted with a four-contact configuration. To increase the ESR signal-to-noise ratio, large GdCuBi<sub>2</sub> single crystals (several mm to cm in size) were crushed into fine powder (~10 μm grain size) to be used in the ESR measurements.

## 3. Results and discussions

Temperature dependent magnetic susceptibility taken for a magnetic field of  $H = 3$  kOe applied parallel ( $\chi_{//}$ ) and perpendicular ( $\chi_{\perp}$ ) to the *c*-axis for a single crystal of GdCuBi<sub>2</sub> is shown in Fig. 1. An antiferromagnetic (AFM) phase transition can be found at  $T_N = 14.3$  K for GdCuBi<sub>2</sub>. In the paramagnetic state, for  $T > 200$  K, Curie-Weiss (CW) linear fits of the inverse of the magnetic susceptibility, shown in the inset of Fig. 1, yield an effective moment  $p = 8.1(2) \mu_B$  for Gd<sup>3+</sup> for both directions, slightly larger than its theoretical value ( $7.94 \mu_B$ ). In addition, the Curie-Weiss temperature  $\theta_{CW} \approx -46$  K ( $\chi_{//}$ ) and  $\theta_{CW} \approx -36$  K ( $\chi_{\perp}$ ) extracted from the CW fits indicate the presence of magnetic frustration, with a frustration parameter  $F = \theta_{CW}/T_N = 3.2$  and 2.5 for the ( $\chi_{//}$ ) and ( $\chi_{\perp}$ ) of GdCuBi<sub>2</sub>, respectively. The temperature dependence of the magnetic susceptibility in similar conditions for the non-magnetic analog LaCuBi<sub>2</sub> is also shown for reference.

The electrical resistivity data as a function of temperature for single crystals of GdCuBi<sub>2</sub> are displayed in Fig. 2, panel 2(a). A linear metallic-like temperature dependence is observed in the paramagnetic state, and an obvious kink can be identified at the  $T_N$  values for all studied crystals. The residual resistivity  $\rho_0$  ranged from 15–40 μΩcm and the RRR values within 2–3.

The magnetic specific heat per mol of Gd divided by temperature ( $C_m/T$ ) and the associated magnetic entropy are presented in panel 2(b) of Fig. 2 ( $2 \text{ K} \lesssim T \lesssim 50 \text{ K}$ ) for GdCuBi<sub>2</sub>. To calculate ( $C_m/T$ ) and the magnetic entropy, the phonon contribution was taken into account using the specific heat data of LaCuBi<sub>2</sub> and subtracted from the total

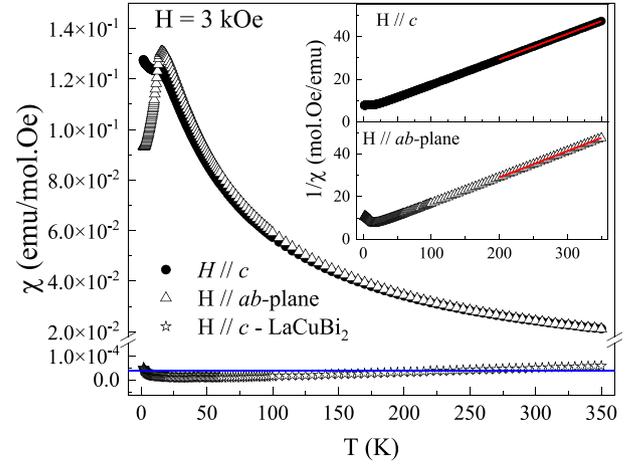


Fig. 1. Magnetic susceptibility as a function of temperature and its inverse (inset) measured with  $H = 3$  kOe applied parallel ( $\chi_{//}$ ) and perpendicular ( $\chi_{\perp}$ ) to the *c*-axis for GdCuBi<sub>2</sub>. The temperature dependence of the magnetic susceptibility with  $H = 3$  kOe applied parallel to the *c*-axis for the non-magnetic analog LaCuBi<sub>2</sub> compound is also shown. The solid blue line is the calculated  $\chi_c \approx 0.04 \times 10^{-3}$  emu/mol (see text) while the red lines in the inset are the Curie-Weiss fittings to the data of GdCuBi<sub>2</sub>.

specific heat of the GdCuBi<sub>2</sub> system. A sharp peak-like anomaly in  $C_m/T$  is observed at  $T_N = 14.3$  K in excellent agreement with the temperature of the appearance of the magnetic susceptibility maximum in Fig. 1. It is possible to identify small additional anomalies in  $C_m/T$  data around 10 K and 4 K that could be associated with a secondary magnetic phase within the ordered state or related to peculiarities of the exchange interaction and small crystal-field splitting, as frequently observed in heat capacity data of Eu<sup>2+</sup> and Gd<sup>3+</sup>-based magnetic intermetallic compounds with  $S = 7/2$  [17,21–24]. Above  $T_N$ , the magnetic entropy reaches the value of  $R \ln 8$ , as expected for the Gd<sup>3+</sup>  $S = 7/2$  multiplet in GdCuBi<sub>2</sub> around 35 K. The fact that  $S$  does not saturate above this temperature is probably related to small discrepancies between the GdCuBi<sub>2</sub> and LaCuBi<sub>2</sub> phonon contributions.

The Gd<sup>3+</sup> ESR powder spectra measured at  $T = 300$  K and the temperature dependence of the Gd<sup>3+</sup> ESR  $\Delta H$  for GdCuBi<sub>2</sub> are displayed in Figs. 3(a) and 3(b), respectively. In the paramagnetic state, for  $T > 250$  K, Dysonian [25] ESR lineshapes expected for localized ESR probes in a lattice with a skin depth smaller than the sample size were measured. By fitting the ESR spectra to the adequate admixture of absorption and dispersion [25], the Gd<sup>3+</sup> ESR  $g$ -value and  $\Delta H$  were extracted for GdCuBi<sub>2</sub>.

For  $T \gtrsim 250$  K, a single ESR line with a roughly temperature independent  $g = 2.177(6)$  was found, and the Gd<sup>3+</sup> ESR linewidth follows a Korringa-like linear thermal broadening as a function of temperature. At lower temperatures, the Gd<sup>3+</sup> ESR  $\Delta H$  starts to broaden. The Gd<sup>3+</sup> ESR  $g$ -value decreases due to the emergence of AFM short-range Gd-Gd magnetic correlations in GdCuBi<sub>2</sub> (inset of Fig. 3(b)). This behavior is typically observed in the paramagnetic state for concentrated Gd- and/or Eu-based magnetically ordered materials [17–21,26]. The high- $T$  linear ESR linewidth thermal broadening was fitted to the expression  $\Delta H = a + bT$ , with  $a = 1760(20)$  Oe and  $b = 1.0(2)$  Oe/K for GdCuBi<sub>2</sub>. Using the simplest approximation to describe the exchange interaction,  $J_{f_s} \mathbf{S}_i \cdot \mathbf{s}_i$ , between a localized  $4f$  electron spin ( $\mathbf{S}$ ) (Gd<sup>3+</sup>) and the free  $ce$ 's spin ( $\mathbf{s}$ ) of the intermetallic host, the ESR  $g$ -shift (Knight shift) [27,28] and the linewidth Korringa rate [29], when “dynamic” and “bottleneck” effects are not significant [30], can be expressed by:

$$4g = J_{f_s} \eta (E_F), \quad (1)$$

and

$$\frac{d(\Delta H)}{dT} = \frac{\pi k}{g\mu_B} J_{f_s}^2 \eta^2 (E_F), \quad (2)$$

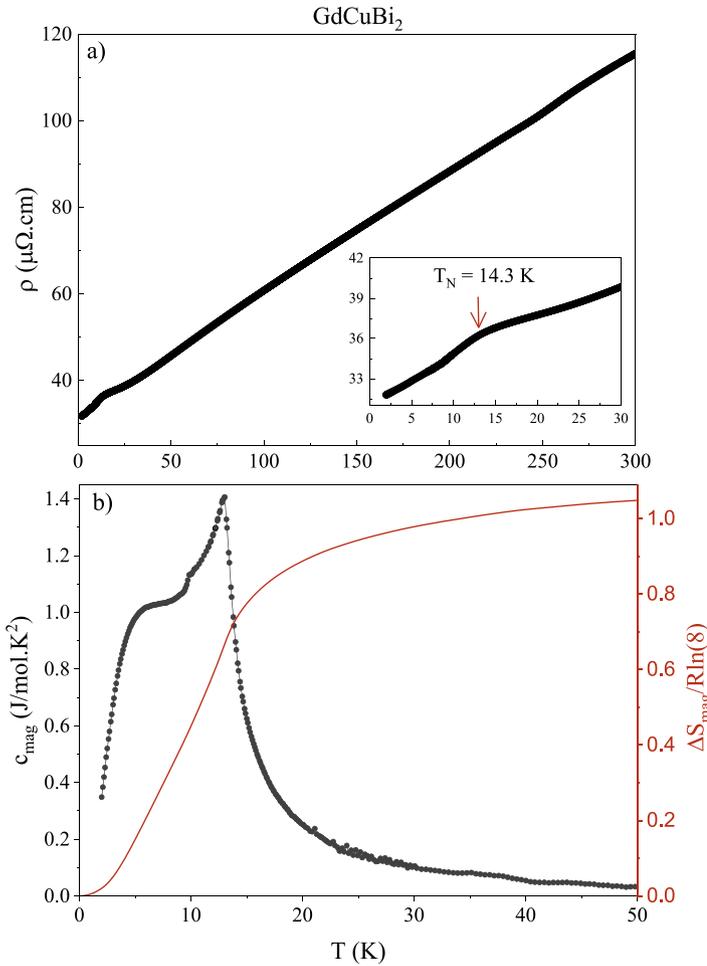


Fig. 2. Temperature dependence of (a) the electrical resistivity measured with the current applied along the [110] direction; (b) the specific heat per mole of Gd divided by temperature and the related magnetic entropy for GdCuBi<sub>2</sub>.

where  $J_{fs}$  is the exchange interaction between the Gd<sup>3+</sup>  $4f$  ESR probes and the  $ce$  in the absence of  $ce$  momentum transfer [31],  $\eta(E_F)$  is the “bare” density of states for one spin direction at the Fermi surface,  $\mu_B$  is the Bohr magneton,  $k$  is the Boltzmann constant and  $g$  is the  $g$ -value for Gd<sup>3+</sup>.

It is important to emphasize that below 350 K, the ESR linewidth starts to broaden significantly due to the spin–spin interaction reaching values much larger than 3 kOe for the  $T < 250$  K. Since this temperature range is not of interest, we choose the scales of Fig. 3(b) to show the Korringa rate at high temperature in greater detail. On the other hand, the  $g$ -value (which is the more accurate information of an ESR experiment) becomes  $T$ -dependent below  $\approx 270$  K, so it is useful to show the  $g$ -value data in a lower temperature range.

Eqs. (1) and (2) are usually employed to describe the ESR data for rare-earths magnetic moments highly diluted in intermetallic hosts with the presence of  $c - e$  spin-flip scattering. In this situation, it might be expected that the relation below would hold:

$$\frac{d(\Delta H)}{dT} = \frac{\pi k}{g\mu_B} (\Delta g)^2, \quad (3)$$

As such, taken the  $g$ -value of Gd<sup>3+</sup> in insulators as 1.993(2) [32],  $(\pi k/g\mu_B) = 2.34 \times 10^4$  Oe/K, the measured  $g$ -shifts and Korringa rate,  $b$ , for the Gd<sup>3+</sup> ESR in GdCuBi<sub>2</sub>, after replacing  $\Delta g \approx 0.184(3)$  in Eq. (3), we extract a thermal broadening of  $\Delta H$ ,  $b \approx 790$  Oe/K. This value is, actually, much larger than the one measured,  $b \approx 1.0(2)$  Oe/K. As such, one can conclude that the simplest treatment used in Eqs.

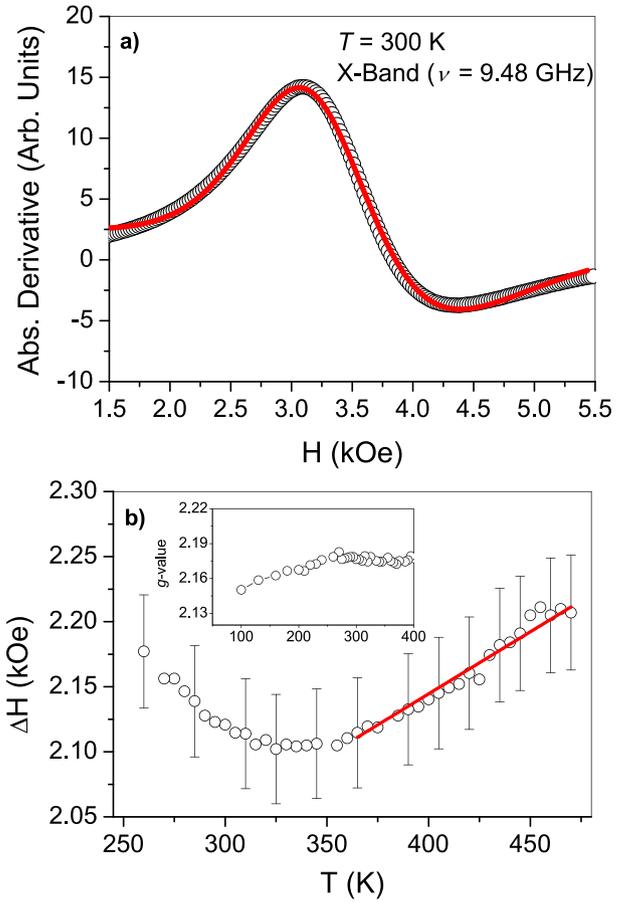


Fig. 3. (a) Gd<sup>3+</sup> ESR powder spectra at  $T = 300$  K with the red solid lines as the best fit of the resonance to a Dyson lineshape. (b) Temperature dependence of the ESR linewidth (and  $g$ -value in the inset) for GdCuBi<sub>2</sub>. The solid red line in (b) is the best fit to  $\Delta H = a + bT$ , yielding  $a = 1760(20)$  Oe and  $b = 1.0(2)$  Oe/K.

1 and 2 are not valid for a dense system such as GdCuBi<sub>2</sub>, and Gd-Gd interactions, conduction electron–electron correlations [33,34],  $\mathbf{q}$ -dependence of the exchange interaction,  $J_{fs}(\mathbf{q})$  [31], and exchange bottleneck effects [30] may need to be considered in the analysis of the ESR data for GdCuBi<sub>2</sub>”.

Therefore, to further analyze our ESR data for GdCuBi<sub>2</sub>, one is required to obtain the “bare” density of states for one spin direction at the Fermi surface,  $\eta(E_F)$  for GdCuBi<sub>2</sub>. Considering a free  $ce$  gas model and using the expression  $\gamma = (2/3)\pi k^2 \eta(E_F)$ ,  $\eta(E_F)$  can be extracted from the specific heat and taken into account the electronic contribution to the specific heat.

However, as can be seen in Fig. 2(b), a significant non-obvious magnon contribution to the low- $T$  specific heat of GdCuBi<sub>2</sub> makes it difficult to estimate the correct  $\gamma$  value from the specific heat of GdCuBi<sub>2</sub>. Alternatively, we have used the specific heat data of LaCuBi<sub>2</sub> [11] to estimate a value for  $\eta(E_F)$  for GdCuBi<sub>2</sub>. This is justified because both Gd<sup>3+</sup> and La<sup>3+</sup> are trivalent, and they similarly contribute with one  $5d$  and two  $6s$  electrons to the conduction band. An electronic specific heat  $\gamma = 2.3(2)$  mJ/mol La-K<sup>2</sup> for LaCuBi<sub>2</sub> [11] yields  $\eta(E_F) = 0.48(5)$  states/eV mol spin. Using this value of  $\eta(E_F)$ , one could extract an electronic spin susceptibility  $\chi_e = 2\mu_B^2 \eta(E_F) \approx 0.04 \times 10^{-3}$  emu/mol. This value of  $\chi_e$  is of the order of the Pauli susceptibility (corrected for the core-diamagnetism) obtained for LaCuBi<sub>2</sub> [11] (see Fig. 1). As such, one can disregard the conduction electron–electron correlations [33,34] in the analyses of our ESR data for GdCuBi<sub>2</sub>.

Considering now the presence of a  $\mathbf{q}$ -dependence of the exchange interaction in an unbottlenecked regime,  $J_{fs}(\mathbf{q})$ , the  $g$ -shift (Eq. (1)) and

the thermal broadening of the linewidth (Eq. (2)) may be re-written as: [30,33–35]

$$\Delta g = J_{fs}(\mathbf{0}) \eta(E_F), \quad (4)$$

and

$$\frac{d(\Delta H)}{dT} = \frac{\pi k}{g\mu_B} \langle J_{fs}^2(\mathbf{q}) \rangle \eta^2(E_F). \quad (5)$$

Using  $\eta(E_F) = 0.48(5)$  states/eV mol spin and Eqs. (4) and (5), we calculated  $J_{fs}(\mathbf{q} = 0) \approx 380$  meV and  $\langle J_{fs}^2(\mathbf{q}) \rangle^{1/2} \approx 3.0$  meV for GdCuBi<sub>2</sub>. This yields an exchange interaction ratio  $[\langle J_{fs}^2(\mathbf{q}) \rangle / J_{fs}^2(\mathbf{0})] \approx 0.008$  for GdCuBi<sub>2</sub>. This value is much smaller than that found for cubic materials [36–38]. The small value of the exchange interaction ratio and the Gd<sup>3+</sup> ESR positive *g*-shift found here suggest a strongly anisotropic (or quasi-2D) Fermi surface, with large *s* and *d*-*ce* contributions for GdCuBi<sub>2</sub>. [39]. In fact, ESR experiments in doped BaFe<sub>2</sub>As<sub>2</sub> could clearly provide evidence of how  $\langle J_{fs}^2(\mathbf{q}) \rangle^{1/2}$  can capture the dimensionality of the electronic bands in real space [39]. In particular, the Eu<sup>2+</sup> ESR Korringa rate and the  $\langle J_{fs}^2(\mathbf{q}) \rangle^{1/2}$  were found to decrease (while  $J_{fs}(0)$  remained nearly constant) as the electronic bands move further away from the Eu<sup>2+</sup> sites in real space as they assume a more planar/*xy*-orbital character. This seems to be the case for the *s* and *d*-*ce* electronic contributions for GdCuBi<sub>2</sub>.

ESR experiments of dilute Gd<sup>3+</sup> in LaCuBi<sub>2</sub> will be valuable to confirm the above results and allow the exchange bottleneck effects to be accounted for. As bottleneck effects are potentially important, the above values should be taken as a lower limit for the values of  $J_{fs}(\mathbf{q})$  and  $\langle J_{fs}^2(\mathbf{q}) \rangle^{1/2}$  in GdCuBi<sub>2</sub>.

The values of  $J_{fs}(\mathbf{q})$  and  $\langle J_{fs}^2(\mathbf{q}) \rangle^{1/2}$  and the strongly anisotropic (or quasi-2D) with large *s* and *d*-*ce* contributions of GdCuBi<sub>2</sub> may help the efforts on the comprehensive study of the magnetic properties and/or the HF behavior along the *R*-112 series, bringing microscopic insights to the understanding of the complex RKKY magnetic interactions found in these series. [2–12].

#### 4. Conclusions

In conclusion, we report temperature-dependent X-Band ( $\nu \sim 9.5$  GHz) Electron Spin Resonance (ESR) on the GdCuBi<sub>2</sub> intermetallic compound. This material is a metallic Curie–Weiss paramagnet at high temperature and evolves to an antiferromagnetic ordered state below  $T_N = 14.3$  K. In the paramagnetic regime, for  $T > 250$  K, a single Dysonian Gd<sup>3+</sup> ESR spectrum with a roughly temperature independent *g*-value is observed for the studied samples. At high-*T*, the Gd<sup>3+</sup> ESR linewidth of the GdCuBi<sub>2</sub> compound follows a Korringa-like temperature dependence. The obtained Korringa rate ( $\Delta H/\Delta T$ ) and *g*-shift ( $\Delta g$ ) from the ESR experiments supported by magnetic susceptibility and specific heat experiments for GdCuBi<sub>2</sub>, allowed us to explore Gd<sup>3+</sup> spin dynamics in this system and extract the exchange parameters between the Gd<sup>3+</sup> ESR probes and the *ce* for this compound. Our results indicate a *q*-dependent exchange interaction ( $J_{fs}(\mathbf{q})$ ) between the Gd<sup>3+</sup> 4*f* and the conduction electrons (*ce*) and exchange bottleneck effects and are likely to be present in GdCuBi<sub>2</sub>. Disregarding the bottleneck effects in the simplest approximation, we could extract the exchange parameters  $J_{fs}(\mathbf{q} = 0) \approx 380$  meV and  $\langle J_{fs}^2(\mathbf{q}) \rangle^{1/2} \approx 3.0$  meV for the Gd<sup>3+</sup> spin dynamics in GdCuBi<sub>2</sub>.

#### CRedit authorship contribution statement

**G.S. Freitas:** Writing – review & editing, Writing – original draft, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **H. Pizzi:** Investigation. **F.B. Carneiro:** Investigation. **M.H. Carvalho:** Investigation. **E.M. Bittar:** Investigation. **E.D. Bauer:** Investigation. **J.D. Thompson:** Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **F. Ronning:** Investigation. **S.M. Thomas:** Investigation. **P.F.S. Rosa:** Supervision,

Resources, Methodology, Investigation, Conceptualization. **S.M. Greer:** Resources, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **P.G. Pagliuso:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Data availability

Data will be made available on request.

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