Evolution of the magnetic properties along the RCuBi₂ (R = Ce, Pr, Nd, Gd, Sm) series of intermetallic compounds

C. B. R. Jesus,[a] M. M. Piva, P. F. S. Rosa, C. Adriano, and P. G. Pagliuso
Instituto de Física "Gleb Wataghin," UNICAMP, 13083-859 Campinas, SP, Brazil

In this paper, the evolution of the magnetic properties along the series of intermetallic compounds RCuBi₂ (R = Ce, Pr, Nd, Gd, Sm) is discussed. These compounds crystallize in a tetragonal ZrCuSi₂ (P4/nmm) structure, and our single crystals of RCuBi₂ grown from Bi-flux show no evidence for Cu-deficiency [Ye *et al.*, Acta Crystallogr. C **52**, 1325 (1996)] as previously reported for R = Ce. For R = Ce, Pr, Gd, and Sm, we found an antiferromagnetic ordering at $T_N \sim 16\,K$, 4.2 K, 13.6 K, and 4.9 K, respectively. For R = Nd, we saw no evidence for a magnetic phase transition down to T = 2 K. These values of T_N clearly show a dramatic breakdown of the De Gennes factor in this series. We discuss our data taken into account the tetragonal crystalline electrical field and the anisotropic Ruderman-Kittel-Kasuya-Yoshida magnetic interaction between the R-ions in this family of compounds. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4860657]

I. INTRODUCTION

The discovery of new series of structurally related compounds with novel physical behavior is an important approach to explore fundamental problems in the physics of highly correlated electron systems. New materials generate unusual properties and nourish the scientific community with complex phenomena, whose understanding leads to scientific improvement. Many metallic systems with rare earth have their macroscopic magnetic and thermal properties significantly influenced by the interaction between the rare-earth ion and the ions in its environment.[2,3]

Systematic studies along the series of rare-earth-based intermetallic compounds are usually of great interest to explore a variety of properties, such as: the interplay between Ruderman-Kittel-Kasuya-Yoshida (RKKY) magnetic interaction, crystalline electrical field (CEF) effects, and Fermi surface (FS) effects commonly present in these materials. Particularly, the series of intermetallic RMIn₅ (115, M = Rh, Ir, Co) (and related compounds) and RM₂T₂ (122 system; M = e.g., Fe, Cu, Ni, Rh, Ru; T = e.g., Si, Ge, As) are interesting examples of systematically studied series that present a large variety of remarkable physical properties such as heavy-fermion (HF) behavior, unconventional superconductivity (SC), and complex magnetic structures.[4–9]

Interestingly, both 115 and 122 series form in tetragonal crystal structure and therefore it is generally believed that such low symmetry structures may favor the occurrence of such remarkable phenomena.

The intermetallic compounds of the family RTBi₂, where T is a transition metal also crystallize in a tetragonal structure with a ZrCuSi₂ structure type (P4/nmm). However, this series has been very little explored in the literature.[1,10] More recently, the CeNi₀.₈Bi₂ compound have attracted great attention due to the reported superconductivity with a superconducting transition temperature $T_c = 4.2\,K$.[11,12] We have successfully synthesized a counterpart series of theses compounds, RCuBi₂ in order to further investigated the physical properties in this series. In a separate publication,[13] we explore the details of the physical properties of our single crystals of CeCuBi₂. These compounds show an antiferromagnetic (AFM) ordering at $T_N \sim 16\,K$, which is higher than the values previously reported for Cu-deficient samples.[1] The magnetic properties of CeCuBi₂ are consistent with an Ising antiferromagnet, and the magnetization data at low temperatures reveal the existence a spin-flop transition when the field is applied along the *c*-axis ($H_c \approx 5$–6 T and T = 2 K; AFM to FM interlayers). The X-ray resonant diffraction data below T_N reveal a commensurate antiferromagnetic structure with propagation vector $(\frac{1}{2}\frac{1}{2}0)$ and the Ce moments oriented along the *c*-axis.[13] In this work, we have investigated the evolution of the magnetic properties along RCuBi₂ (R = Ce, Pr, Nd, Gd, Sm) by means of magnetic susceptibility, electrical resistivity, and heat capacity measurements in single crystals grown from Bi-flux. The behavior of antiferromagnetic ordering temperature T_N shows a dramatic breakdown of the De Gennes factor in this series.

II. EXPERIMENT

Single crystalline samples of the RCuBi₂ (R = Ce, Pr, Nd, Gd, Sm) compounds were grown using metallic flux technique[14] with starting composition R:Cu:Bi = 1:1:20. The crucible containing the elements was cover with quartz wool and sealed inside an evacuated quartz tube. The tube was placed in a furnace and heated up to 1050 °C with a rate of 50 °C/h. After 4 h at 1050 °C, the batch was subjected to a slow cooling of 5 °C/h down to 350 °C. The excess Bi flux was then spun in a centrifuge and platelets-like crystals were mechanically removed from the crucible. Typical crystal sizes were 3.0 mm × 3.0 mm × 0.1 mm. The crystal structure

[a]Electronic mail: edbruno@ifi.unicamp.br.

TABLE I. Experimental parameters for RCuBi$_2$ (R = Ce, Pr, Nd, Gd, Sm).

	a (Å)	c (Å)	T_N (K)	μ_{eff} (μ_B)	θ_p (K)
CeCuBi$_2$	4.555(4)	9.777(8)	16	2.5(1)	≈ -16
PrCuBi$_2$	4.534(4)	9.770(8)	4.2	3.61(1)	≈ -5
NdCuBi$_2$	4.524(4)	9.964(8)		3.4(1)	≈ -11
SmCuBi$_2$	4.452(4)	9.653(8)	4.9		
GdCuBi$_2$	4.488(4)	9.694(8)	13.6	8.03(1)	≈ -36

and phase purity were determined by x-ray powder diffraction. These compounds crystallize in a tetragonal ZrCuSi$_2$ structure and their lattice parameters are given in Table I. Magnetic susceptibility measurements as function of the temperature were carried out using a SQUID magnetometer (Quantum Design MPMS5). Specific-heat measurements were performed on a Quantum Design PPMS small-mass calorimeter, and electrical resistivity was measured using a low-frequency ac resistance bridge and four-contact configuration.

III. RESULTS AND DISCUSSION

Figure 1 presents the temperature dependence of the magnetic susceptibility, for $H = 1$ kOe within the temperature range of $2\,\mathrm{K} < T < 300\,\mathrm{K}$ along the c-axis, $\chi_\parallel$, and in the ab-plane, $\chi_\perp$, for the RCuBi$_2$ (R = Ce, Pr, Nd, Gd, Sm) compounds. For R = Ce, Pr, Gd, and Sm, we found an antiferromagnetic ordering at $T_N \sim 16$ K, 4.2 K, 13.6 K, and 4.9 K, respectively. For R = Nd, we saw no evidence for a magnetic phase transition down to T = 2 K. From Curie-Weiss linear fits to χ^{-1} poly-crystalline average (see inset of Fig. 1) in the
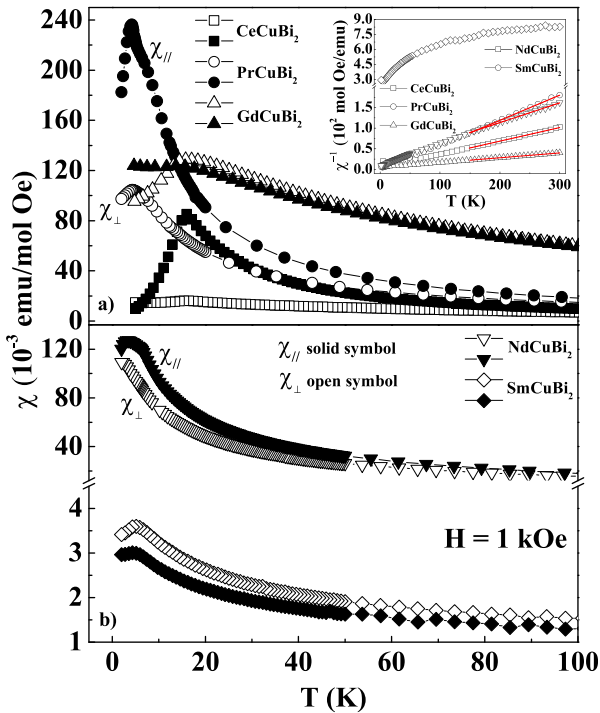
range of 150–300 K, we have extracted the Curie-Weiss temperature (θ_{CW}) and the effective magnetic moment (μ_{eff}) for all compounds, except for R = Sm, which are in agreement with the theoretical values (see Table I). In the Sm-based case, the high temperature magnetic anisotropy is probably associated with CEF in both ground $J = 5/2$ and excited $J = 7/2$ multiplet states of the Sm^{3+} ion.[15] As typical in Sm-based materials, the high-T behaviour of the inverse of magnetic susceptibility does not show a linear temperature dependence due to a Van Vleck contribution (which complicates the extraction of μ_{eff} and θ_p from these data).[15]

Figure 2 shows the magnetic contribution to the specific heat divided by temperature in the temperature range of $2\,\mathrm{K} \lesssim T \lesssim 30\,\mathrm{K}$, for RCuBi$_2$ (R = Ce, Pr, Nd, Gd, Sm). To obtain the magnetic contribution to the specific heat, the phonon contribution was subtracted from the original data using the specific heat data of non-magnetic LaCuBi$_2$ compound. The peak-like anomaly in C_m/T corresponding to the onset of AFM order can be seen at $T_N \sim 16$ K, 4 K, 13 K, and 4.9 K, for CeCuBi$_2$, PrCuBi$_2$, GdCuBi$_2$, and SmCuBi$_2$, respectively; for NdCuBi$_2$, we saw no evidence for a magnetic phase transition down to T = 2 K [Fig. 2]. The Néel temperatures obtained from the specific heat data are in very good agreement with the magnetic susceptibility data (see Figures 1(a) and 1(b)).

The T-dependence of the electrical resistivity measured for RCuBi$_2$ (R = Ce, Pr, Nd, Gd, Sm) single crystals is shown in Figure 3. The high temperature data show a metallic behavior for these compounds. At low temperatures, subtle features can be seen at the respective ordering temperatures for all compounds with exception of the NdCuBi$_2$ compound which consistently shows no phase transition down to T = 2 K.

In order to discuss the evolution of the magnetic properties of the RCuBi$_2$ (R = Ce, Pr, Nd, Gd, Sm) compounds, we plot in Figure 4 the T_N values obtained for the studied compounds along the R-earth series, normalized by its value for GdCuBi$_2$ ($T_N = 13.6$ K), where we used $T_N < 2$ K for NdCuBi$_2$ for completeness.

The solid lines in Fig. 4 are the de Gennes factor $(g_J^2 - 1)(J(J + 1))$ for ground state multiplet J through the
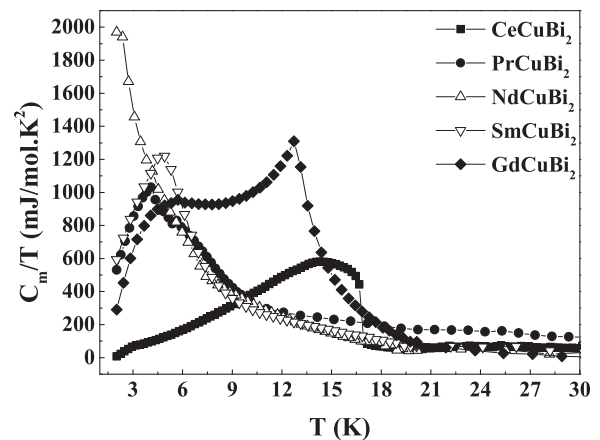

FIG. 1. Temperature dependence of the magnetic susceptibility, for applied field H along the c-axis, $\chi_\parallel$ (open symbols), and in the ab-plane, $\chi_\perp$ (solid symbols), for RCuBi$_2$ (R = Ce, Pr, Nd, Gd, Sm) materials (a) for R = Ce, Pr, and Gd and (b) for R = Nd and Sm.

FIG. 2. The magnetic contribution to the specific heat data divided by temperature in the temperature range $2\,\mathrm{K} \lesssim T \lesssim 30\,\mathrm{K}$ for RCuBi$_2$ (R = Ce, Pr, Nd, Gd, Sm).
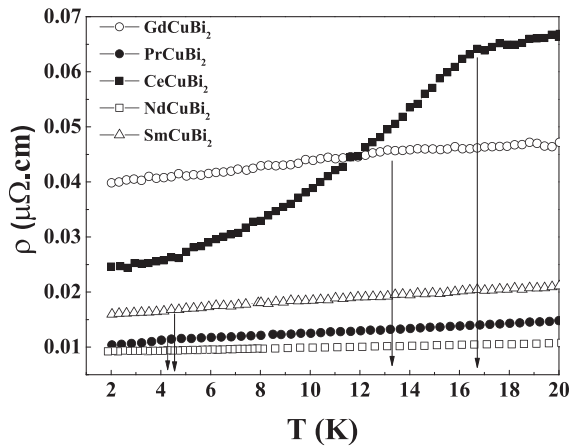
FIG. 3. Temperature dependence of the electrical resistivity for RCuBi$_2$ (R = Ce, Pr, Nd, Gd, Sm) single-crystals. The solid arrows point out the Néel Temperatures for the compounds
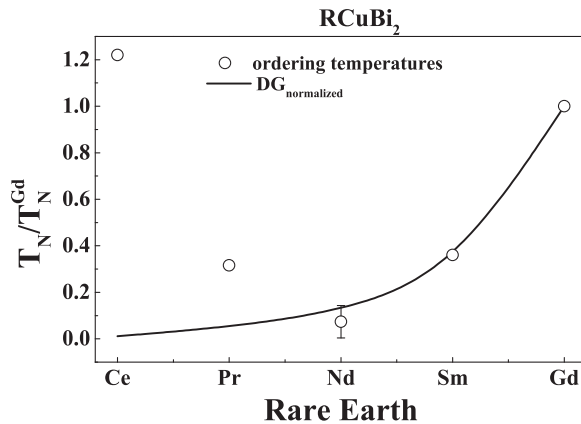

FIG. 4. T_N values normalized to the T_N of GdCuBi$_2$ and plotted through the rare-earth series for the RCuBi$_2$ (R = Ce, Pr, Nd, Gd, Sm) compounds. The solid line is the de Gennes factor $[(g_J^2 - 1)(J(J + 1))]$ for ground-state multiplet J of the rare earths normalized by its value for GdCuBi$_2$.

rare-earths. If one normalizes the de Gennes line to the GdCuBi$_2$ T_N value, the Sm-based T_N value sits reasonably on the line but the T_N values for the R = Ce, Pr, and Nd do not follow a de Gennes scaling. In fact, the upper limit $T_N < 2$ K for the R = Nd compound is below de Gennes line, while the actual values T_N for R = Ce and Pr are drastically above de Gennes lines.

De Gennes scaling[16] does not take into account CEF, Kondo effects and/or spatial dependence, and anisotropic effects in the effective exchange parameter. Some of these effects are expected to be present in the RCuBi$_2$ series. Therefore, it is not a surprise that the T_N values for complex rare-earth series in low-symmetry structure. In fact, it has been shown for R$_m$MIn$_{3m+2}$ (M = Rh, Ir, and Co; m = 1, 2) complex classes of intermetallic compounds that the tetragonal CEF parameters strongly affects the RKKY interaction dominantly and determines the direction of the ordered moments and the behavior of the ordering temperature for these series.[7–9,17,18]

The particular case where the l-ordered moments lie in along the c-axis T_N can be enhanced by tuning the CEF

parameters.[7–9,17,18] This is certainly the case of CeCuBi$_2$, for which x-ray resonant diffraction data revealed an commensurate antiferromagnetic structure with propagation vector $\left(\frac{1}{2}\frac{1}{2}0\right)$ and the Ce moments oriented along the *c*-axis.[13]

As such, further investigation and direct determination of the tetragonal CEF parameters along these series is in progress and it will be valuable to confirm the CEF effects in the antiferromagnetic interaction within the and RCuBi$_2$ series.

IV. CONCLUSIONS

In conclusion, we report the evolution of the magnetic properties along the series of intermetallic compounds RCuBi$_2$ (R = Ce, Pr, Nd, Gd, Sm). Enlightened by our macroscopic measurements, we found a dramatic breakdown of the De Gennes scaling in this series. We interpreted data suggesting a CEF include entrancement with T_C for R = Ce and Pr compounds.

ACKNOWLEDGMENTS

[1]J. Ye, Y. K. Huang, K. Kadowari, and T. Matsumoto, Acta Crystallogr. C **52**, 1325 (1996).
[2]E. Segal and W. E. Wallace, J. Solid State Chem. **2**, 347 (1970).
[3]J. Jensen and A. R. Mackintosh, *Rare Earth Magnetism: Structures and Excitations* (Clarendon Press, Oxford, 1991).
[4]A. Szytula, Mater. Sci.-Poland **24**, 737 (2006).
[5]H. v. Löhneysen, A. Rosch, M. Vojta, and Wölfle, Rev. Mod. Phys. **79**, 1015 (2007).
[6]J. D. Thompson and Z. Fisk, J. Phys. Soc. Jpn. **81**, 011002 (2012).
[7]P. G. Pagliuso, J. D. Thompson, M. F. Hundley, and J. L. Sarrao, Phys. Rev. B **62**, 12266–12270 (2000).
[8]P. G. Pagliuso, J. D. Thompson, M. F. Hundley, J. L. Sarrao, and Z. Fisk, Phys. Rev. B **63**, 054426 (2001).
[9]P. G. Pagliuso, D. J. Garcia, E. Miranda, E. Granado, R. Lora-Serrano, C. Giles, J. G. S. Duque, R. R. Urbano, C. Rettori, J. D. Thompson *et al.*, J. Appl. Phys. **99**, 08P703 (2006).
[10]A. Thamizhavel, A. Galatanu, E. Yamamoto, T. Okubo, M. Yamada, K. Tabata, T. C. Kobayashi, N. Nakamura, K. Sugiyama, K. Kindo, T. Takeuchi, R. Settai, and Y. Onuki, J. Phys. Soc. Jpn. **72**, 2632 (2003).
[11]H. Mizoguchi, S. Matsuishi, M. Hirano, M. Tachibana, E. Takayama-Muromachi, H. Kawaji, and H. Hosono, Phys. Rev. Lett. **106**, 057002 (2011).
[12]K. Kodama, S. Wakimoto, N. Igawa, S. Shamoto, H. Mizoguchi, and H. Hosono, Phys. Rev. B **83**, 214512 (2011).
[13]C. Adriano *et al.*, "Physical properties and magnetic structure of CeCuBi$_2$ intermetallic compound" (unpublished).
[14]Z. Fisk and J. P. Remeika, in *Handbook on the Physics and Chemistry of Rare Earth*, edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier Science Publishers, Amsterdam, 1989), Vol. 12, p. 53.
[15]K. H. J. Buschov, H. W. de Wijn, and M. Van Diepen, J. Chem. Phys. **50**, 137 (1969).
[16]P. G. De Gennes, Compt. Rend. **247**, 1836 (1958); J. Physique Rad. **23**, 510 (1962); B. Coqblin, *The Electronic Structure of Rare–Earth Metal and Alloys: The Magnetic Heavy Rare–Earths* (Academic Press, New York, 1977).
[17]R. Lora-Serrano, D. J. Garcia, E. Miranda, C. Adriano, C. Giles, J. G. S. Duque, and P. G. Pagliuso, Phys. Rev. B **79**, 024422 (2009).
[18]R. Lora-Serrano, C. Giles, E. Granado, D. J. Garcia, E. Miranda, O. Aguero, L. M. Ferreira, J. G. S. Duque, and P. G. Pagliuso, Phys. Rev. B **74**, 214404 (2006).