

Electron spin resonance g shift in Gd_5Si_4 , Gd_5Ge_4 , and $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$

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(Received 23 November 2005; revised manuscript received 30 January 2006; published 4 April 2006)

Gd_5Si_4 , Gd_5Ge_4 , and $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$ compounds were studied by electron spin resonance. The arc-melted samples were initially characterized by optical metallography, x-ray diffraction, and static magnetization measurements. The electron spin resonance results show a negative paramagnetic g shift for Gd_5Si_4 and $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$, and a smaller positive one for Gd_5Ge_4 . The values of the exchange parameter (j) between the localized Gd-4*f* spins and the conduction electrons are obtained from the g shifts. These values are positive and of the same order of magnitude for Gd_5Si_4 and $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$, and negative one order of magnitude smaller for Gd_5Ge_4 . The electron spin resonance data were interpreted considering the strongly bottlenecked solution of the coupled Bloch-Hasegawa equations.

DOI: [10.1103/PhysRevB.73.144404](https://doi.org/10.1103/PhysRevB.73.144404)

PACS number(s): 75.30.Sg, 76.50.+g, 81.05.Bx, 81.40.Rs

I. INTRODUCTION

Since the first reports on the giant magnetocaloric effect (GMCE) in $\text{Gd}_5\text{Ge}_2\text{Si}_2$ and related alloys,^{1,2} it was clear that to understand the complexity of their magnetic behavior a detailed description of the electronic structure is crucial. The subsequent proposed explanations^{3,4} for the exchange mechanisms and experimental accounts^{5,6} have provided the understanding of important aspects, but could be still more explored with a detailed knowledge of the electronic structure. Theoretical works employing local spin-density approximation (LSDA+ U)⁷ and tight binding linear muffin-tin orbital method (TB-LMTO)⁸⁻¹⁰ have been used to obtain the electronic structure, magnetic moments, and exchange coupling parameters for $\text{Gd}_5\text{Ge}_2\text{Si}_2$, Gd_5Si_4 , and Gd_5Ge_4 . The predicted band structures for Gd_5Si_4 and Gd_5Ge_4 presented good agreement with ultraviolet photoelectron spectroscopy and resistivity measurements.^{8,9} Furthermore, a qualitative description of the magnetic behavior of these alloys could be done based on the predicted exchange coupling parameters.¹¹ In a previous work¹² characterization of the phase transitions of $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$ samples has been made correlating magnetization and electron spin resonance (ESR) results. We note that this particular stoichiometry lends the sample to be constituted of two crystallographic phases, the majority one with the 5:2:2 type structure, and a minority one with $\text{GdGe}_{0.64}\text{Si}_{0.6}$ stoichiometry (corresponding to the 1:1 binary phase). This is a consequence of the peritectic formation of the 5:2:2 compound.^{13,14} The results of the magnetic analysis show that the 5:2:2 stoichiometry (phase) is comprised of two coexisting magnetic allotropic phases, the majority one with monoclinic structure that presents the first-order magnetic transition with Curie temperature of 268 K, and a minority one with an orthorhombic structure, showing a second-order magnetic transition at 302 K. One estimate of the relative amounts of these phases, as inferred from magnetization measurements,¹¹ is $\sim 80\%$ for the monoclinic and $\sim 20\%$ for the orthorhombic one. The ESR results permitted a clear distinction of the two coexisting magnetically ordered phases in the temperature range between the two observed

magnetic phase transitions. The second ESR signal was associated with the orthorhombic allotropic phase of the 5:2:2 stoichiometry.

In this work we present ESR measurements on Gd_5Si_4 , Gd_5Ge_4 , and $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$ compounds. Special attention is given to the behavior of the effective g values (g_{eff}) in the paramagnetic regime in order to explain it in terms of the electronic structure. This was done using the model presented by Zipper¹⁵ and the predicted band structures.⁷⁻⁹ The exchange coupling constant (j) between the localized electron spins (Gd-4*f*) and the conduction electron spins is derived from the measured g_{eff} values.

The compounds of the family $\text{Gd}_5(\text{Ge}_{1-x}\text{Si}_x)_4$ with $x < 0.2$ are antiferromagnetic (for some temperature range) while the ones with $x > 0.2$ are ferromagnetic. The Gd-Gd distances inside the slabs (layers) which constitute the material,¹⁻³ do not change significantly when one passes from the compounds with $x < 0.2$ to the $x > 0.2$ compositions. Then the intraslab Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction would be practically the same. As the RKKY interaction depends not only on the ion-ion distances but also on the square of j ,¹⁶ our results for this parameter indicate a remarkable distinction between the Gd_5Ge_4 overall exchange and the interactions present in the Gd_5Si_4 and $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$ compounds. Nevertheless, this may not explain the low temperature antiferromagnetic character of the Gd_5Ge_4 compound. Therefore, additional interslab interactions such as the dipolar or the superexchange ones⁴ should be considered.

II. EXPERIMENTAL

The samples were arc-melted three times under Ar atmosphere using 99.9 wt. % Gd and electronic grade (99.9999% purity) Ge and Si. The phase composition of the samples has been checked by optical metallography and x-ray diffraction analysis. Gd_5Ge_4 is monophasic within the x-ray diffraction experimental accuracy, but $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$ and Gd_5Si_4 present additional minority phases. As discussed above, the $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$ sample presents a small amount of the

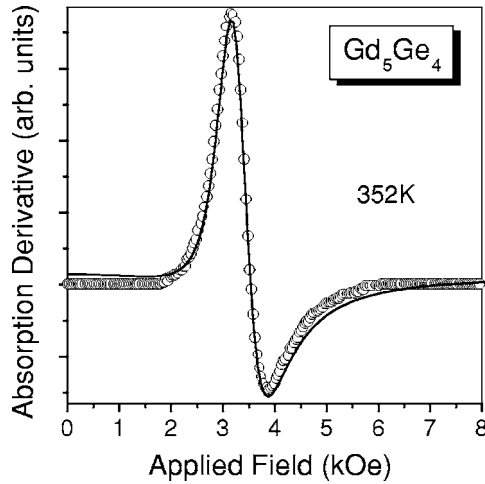


FIG. 1. Typical ESR spectrum obtained for Gd_5Ge_4 . The line is the Dysonian fit to the experimental data (open circles).

phase $\text{GdGe}_{0.4}\text{Si}_{0.6}$ and also a small quantity of the orthorhombic allotropic modification of the 5:2:2 phase. The Gd_5Si_4 sample also presents a small amount of the GdSi phase, due to its peritectic mode of formation.¹⁴ Magnetic and x-ray measurements obtained respectively with a commercial superconducting quantum interference device (SQUID) magnetometer and diffractometer showed good agreement with the published data. The magnetic transition temperatures are 123 ± 4 K for Gd_5Ge_4 , 338 ± 2 K for Gd_5Si_4 , 302 ± 2 K and 266 ± 1 K for $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$, as determined from the magnetization curves (applied magnetic field of 200 Oe).

The ESR measurements were carried out on a spectrometer operating around 9.29 GHz and at temperatures between 105 K and 405 K. The temperature in a TE_{102} resonance cavity was controlled by N_2 gas flux and the uncertainty in the determination of the sample temperature was smaller than 2 K.

Figure 1 presents a representative ESR spectrum for Gd_5Ge_4 obtained above the ordering temperature. All spectra have been well fitted with a Dysonian curve, which is the typical shape for paramagnetic resonance lines of metallic samples. The measured A/B ratios of low field to high field peak heights are close to the theoretical value (2.55) for samples much larger than the skin depth. Approaching the magnetic transitions, this line shape is distorted as a consequence of the increasing short-range ordering effects. From the spectral fits, the ESR amplitude, linewidth (ΔH), and external field for resonance are obtained. The last parameter is used to calculate the effective g value.

III. ESR MEASUREMENTS

The behavior of ΔH in the paramagnetic regime has the expected characteristics for high concentration magnetic metals, showing a minimum value above the ordering temperature, and then increasing linearly with temperature. The slope of ΔH in the linear region is about 1.5 Oe/K and 2 Oe/K for Gd_5Ge_4 and $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$, respectively. For Gd_5Si_4 the linear behavior was not reached at the available experimental maximum temperature.

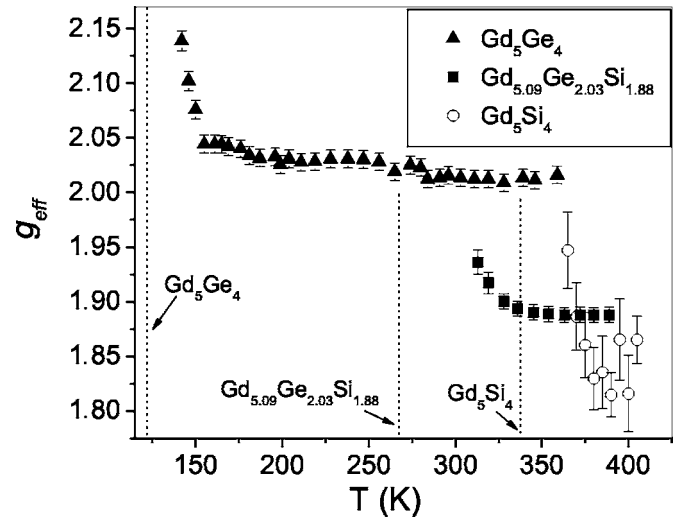


FIG. 2. Effective g values in the paramagnetic regime obtained for the three studied compounds. The dotted lines indicate the order temperatures for each sample.

The paramagnetic effective g values for each sample are shown in Fig. 2. Their variations as a function of temperature have similar aspects with a tendency to a constant value at high temperatures and an upturn when temperature decreases towards the transition temperature (T_T). However, for Gd_5Si_4 the experimentally available maximum temperature is not enough to show so clearly the constant value of g_{eff} . The constant values for each compound are shown in Table I. The value for Gd_5Si_4 was obtained extrapolating the g_{eff} versus T curve to high temperatures. In the case of $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$ one should still consider the possible influence of the second-order transition (302 K) in the verified upturn. Considering the g value for noninteracting Gd ions in insulating samples ($g_o = 1.992$), the main aspects to be noted with respect to the high temperature constant values are (i) Gd_5Si_4 and $\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$ present a negative g shift ($g_{eff} < g_o$) while Gd_5Ge_4 presents a positive one; and (ii) the absolute value of the shift for Gd_5Ge_4 is rather smaller than for the other two compositions, which are close to each other.

In an ESR experiment with paramagnetic metals, the main magnetic relaxation process is the scattering of the conduction electrons, or in different words, the energy transfer from the excited spin system ($4f$ spin of the Gd^{3+} ions in our case) to the conduction electron system (d -type⁶⁻⁹). Usually, in concentrated magnetic alloys the amount of electrons avail-

TABLE I. ESR stable effective g factors, calculated exchange spin-conduction electron parameter, and bandwidths used in the calculation of j . The intervals of j values correspond to ξ from 0.3 to 0.2 eV.

Compound	$g_{eff} (T \gg T_T)$	j (eV)	$\Delta\epsilon$ (eV)
Gd_5Si_4	1.82 ± 0.06	0.47 to 0.72	2 ^a
$\text{Gd}_{5.09}\text{Ge}_{2.03}\text{Si}_{1.88}$	1.888 ± 0.002	0.28 to 0.43	1.9 ^b
Gd_5Ge_4	2.02 ± 0.04	-0.05 to -0.08	1.3 ^c

^aRef. 8.

^bRef. 9.

^cRefs. 7 and 8.

able to take part in the relaxation process is relatively small and such shortage modifies the whole process, leading to the so-called bottleneck effect.^{15,17,18} The most straightforward method to include these aspects in the treatment of ESR is to solve two coupled Bloch-Hasegawa dynamic equations, one for the motion of each magnetization, namely the spin magnetization and the conduction electron one. From the solutions it is possible to obtain Eq. (1) (see below) for the effective g factor in the strong bottlenecked limit.^{15,16} Although these coupled Bloch-Hasegawa equations can be obtained in a phenomenological way, they can be deduced from *ab initio* quantum arguments if second-order terms are dropped out of the dynamic susceptibilities.¹⁷ Such a simplification in the model is equivalent to using the molecular-field approximation, and this is the reason why Eq. (1) is employed to discuss the g_{eff} values only at the limit of stability above the transition temperature (T_T), $T \gg T_T$.

Considering the measured g shifts and the slopes of the linear part of the ΔH versus T curve, we verified that the simple Korringa relation for ΔH (Refs. 15–17 and 19) is not satisfied for our samples. However, the low values observed for these slopes can be explained assuming that the samples are strongly bottlenecked and using the adequate expression for ΔH (Refs. 16 and 20) (the manifestation of the bottleneck effect had already been proposed for $Gd_{5.09}Ge_{2.03}Si_{1.88}$).¹² Therefore, for the samples studied here, Eq. (1) is a good approximation to interpret our ESR results.

$$g_{eff} \approx g_o + (g_e - g_o) \left(\frac{g_o}{g_e} \right)^2 \frac{\chi_e}{\chi_s} \left(1 + \frac{g_e}{g_o} \lambda \chi_s \right), \quad (1)$$

where g_e represents the conduction electron g factor, λ is $2j/(g_e g_o)$, and χ_e and χ_s are the Pauli and ion susceptibility, respectively.

The general model with the Bloch-Hasegawa equations involves several relaxation parameters still not known for the $Gd_5(Ge_{1-x}Si_x)_4$ family of compounds. The solutions presented by Zipper¹⁵ are convenient, as the approximations done along the calculations allow one to write the g_{eff} in terms of the bottleneck parameter, and not the relaxation rates explicitly. The strong bottlenecked limit correspond to the case for which this parameter is much smaller than 1, and the solution reduces to Eq. (1). Also according to Zipper, the g factor for d -character conduction electrons differs from the free electron value in the form of Eq. (2),

$$g_e \approx 2(1 - \xi/\Delta\varepsilon), \quad (2)$$

where ξ is the mean spin-orbit energy of the electrons and $\Delta\varepsilon$ is the width of the conduction band (hybridized s - p - d band, but with the main contribution coming from Gd d electrons). This result comes from treating the d electron energy under the action of the lattice potential as an unperturbed system, and including the spin-orbit coupling and the external magnetic field as perturbations. Experimental values for these parameters are not available for the $Gd_5(Ge_{1-x}Si_x)_4$

family, but electronic structure calculations have already been done.^{6–9} In this way we have used the values of $\Delta\varepsilon$ and of the density of states obtained theoretically together with the measured g_{eff} to obtain the values of j presented in Table I. The bandwidths were estimated from those electronic structures considering the energy intervals between the pseudogap below the Fermi energy and the first deep valley above. For $Gd_{5.09}Ge_{2.03}Si_{1.88}$ we used in the calculations the parameters obtained for the similar composition $Gd_5Ge_2Si_2$, whose electronic structure calculation is available in the literature.^{6,9}

From theoretical and experimental works on metallic compounds with rare-earth elements,^{21–23} one can expect that ξ is between 0.2 eV and 0.3 eV for the three compounds studied here. Assuming these values, one can see (Table I) that j is positive for Gd_5Si_4 and $Gd_{5.09}Ge_{2.03}Si_{1.88}$, but negative for Gd_5Ge_4 . Furthermore, the j value for Gd_5Si_4 is larger than that for $Gd_{5.09}Ge_{2.03}Si_{1.88}$, and both are rather larger, in absolute values, than the one for Gd_5Ge_4 . Not surprisingly these results point to intrinsic differences between the two first compositions and Gd_5Ge_4 . As the RKKY is proportional to the square of j , these results are compatible with the fact that Gd_5Si_4 and $Gd_{5.09}Ge_{2.03}Si_{1.88}$ order at high temperatures while Gd_5Ge_4 orders at about 123 K.

IV. CONCLUSIONS

The magnetic behavior of $Gd_5(Ge_{1-x}Si_x)_4$ is practically the same from $x=0.5$ to $x=1$, but it presents several important changes for $0 \leq x \leq 0.5$. In particular, there are marked changes for $x < 0.2$ compositions (see, e.g., Refs. 2, 5, 7, and 8), whose properties result from variations of both crystalline and electronic structure. The predicted displacement of the Fermi level to an energy closer to the low pseudogap of the conduction band is one important alteration occurring for $x \rightarrow 0$. The results obtained for j in this work show another important intrinsic change accompanying the crystalline and electronic transformations: For $x < 0.2$ the $4f$ -conduction electrons exchange is drastically altered. This naturally affects the electron magnetic polarization and consequently the Gd-Gd interaction, which varies with the square of j . The consequent lower value of the RKKY interaction in Gd_5Ge_4 can be an additional aspect, besides the absence of interslab bounds, providing an environment in which other interactions between the slabs become important, such as the dipolar one.

ACKNOWLEDGMENTS

The authors are grateful to G. Samolyuk for helpful discussions about the electronic structure calculations and F. C. G. Gandra for discussions about the bottleneck effect. This work has been supported by CNPq, FAPESP, and FAEP-UNICAMP, Brazilian agencies. MJMP and AMGC are grantees of the CAPES Foundation.

- ¹V. K. Pecharsky and K. A. Gschneidner, Jr., *Phys. Rev. Lett.* **78**, 4494 (1997).
- ²V. K. Pecharsky and K. A. Gschneidner, Jr., *J. Alloys Compd.* **260**, 98 (1997).
- ³W. Choe, V. K. Pecharsky, A. O. Pecharsky, K. A. Gschneidner, Jr., V. G. Young, Jr., and G. J. Miller, *Phys. Rev. Lett.* **84**, 4617 (2000).
- ⁴E. M. Levin, V. K. Pecharsky, and K. A. Gschneidner, Jr., *Phys. Rev. B* **62**, R14625 (2000).
- ⁵J. Szade and G. Skorek, *J. Magn. Magn. Mater.* **196-197**, 699 (1999).
- ⁶E. M. Levin, V. K. Pecharsky, K. A. Gschneidner, Jr., *Phys. Rev. B* **60**, 7993 (1999).
- ⁷B. N. Harmon and V. N. Antonov, *J. Appl. Phys.* **91**, 9815 (2002).
- ⁸E. M. Levin, V. K. Pecharsky, K. A. Gschneidner, Jr., G. J. Miller, *Phys. Rev. B* **64**, 235103 (2001).
- ⁹G. Skorek, J. Deniszczyk, and J. Szade, *J. Phys.: Condens. Matter* **14**, 7273 (2002).
- ¹⁰G. D. Samolyuk and V. P. Antropov, *J. Appl. Phys.* **91**, 8540 (2002).
- ¹¹V. K. Pecharsky, G. D. Samolyuk, V. P. Antropov, A. O. Pecharsky, and K. A. Gschneidner, Jr., *Solid State Chem.* **171**, 57 (2003).
- ¹²M. J. M. Pires, A. Magnus G. Carvalho, S. Gama, E. C. da Silva, A. A. Coelho, and A. M. Mansanares, *Phys. Rev. B* **72**, 224435 (2005).
- ¹³S. Gama, C. S. Alves, A. A. Coelho, C. A. Ribeiro, A. I. C. Persiano, and Dailto Silva, *J. Magn. Magn. Mater.* **272-276**, 848 (2004).
- ¹⁴N. I. Usenko, M. I. Ivanov, V. V. Berezutski, and R. I. Polotska, *J. Alloys Compd.* **266**, 186 (1998).
- ¹⁵E. Zipper, *J. Phys. F: Met. Phys.* **12**, 3123 (1982).
- ¹⁶W. S. Glaunsinger, *J. Phys. Chem. Solids* **37**, 51 (1976).
- ¹⁷K. Kaczmarek, *J. Alloys Compd.* **240**, 88 (1996).
- ¹⁸S. E. Barnes, *Adv. Phys.* **30**, 801 (1981).
- ¹⁹R. H. Taylor and B. R. Coles, *J. Phys. F: Met. Phys.* **5**, 121 (1975).
- ²⁰K. Kaczmarek, E. Kwapulińska, A. Ślebarski, E. Zipper, and A. Chelkowski, *J. Magn. Magn. Mater.* **50**, 101 (1985).
- ²¹G. Schütz, M. Knülle, R. Wienke, W. Wilhelm, W. Wagner, P. Kienle, and R. Frahm, *Z. Phys. B: Condens. Matter* **73**, 67 (1988).
- ²²J. W. Kim, Y. Lee, D. Wermeille, B. Sieve, L. Tan, S. L. Bud'ko, S. Law, P. C. Canfield, B. N. Harmon, and A. I. Goldman, *Phys. Rev. B* **72**, 064403 (2005).
- ²³Y. Lee, J. W. Kim, A. I. Goldman, and B. N. Harmon, *J. Appl. Phys.* **97**, 10A311 (2005).