Electron scattering processes in $\text{Ho}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds: Electrical resistivity studiesA. M. Pereira,^{1,*} J. P. Araújo,¹ J. R. Peixoto,¹ M. E. Braga,¹ P. A. Algarabel,^{2,3} C. Magen,^{4,3} L. Morellón,^{3,5} M. R. Ibarra,^{3,5} and J. B. Sousa¹¹*IFIMUP and IN-Institute of Nanoscience and Nanotechnology, Departamento de Física da Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, P-4169-007 Porto, Portugal*²*Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza and Consejo Superior de Investigaciones Científicas, E-50009 Zaragoza, Spain*³*Departamento de Física de la Materia Condensada, Universidad de Zaragoza, Spain*⁴*Instituto de Nanociencia de Aragón-ARAIID, Universidad de Zaragoza, E-50009 Zaragoza, Spain*⁵*Instituto de Nanociencia de Aragón, Universidad de Zaragoza, E-50009 Zaragoza, Spain*

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We present a detailed study of the temperature dependence of the electrical resistivity [$\rho(T)$] in the range 13–300 K for the $\text{Ho}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system. Three distinct $\rho(T)$ behaviors are observed, associated with different magnetic and crystallographic structures along the series. In the samples with an antiferromagnetic phase (AFM) one observes a shoulder near the Néel temperature (T_N) attributed to the formation of a gap on the Fermi surface. This gap is analyzed using a phenomenological two-band model for an AFM with distinct atomic and magnetic periodicities, and its effect seems to extend well above T_N . We also found the presence of short-range magnetic clusters in the paramagnetic (PM) phase. On the ferromagnetic (FM) materials, the distinct $\rho(T)$ scattering contributions (phonon, magnetic, and residual terms) are extracted from the measurements, with $\rho(T)$ mainly dominated by electron spin scattering. An additional contribution is also observed, arising from the strong crystal field effect in these materials. The effect is mainly observed in the PM phase, leading to a curvature on $\rho(T)$ in this phase. Using a two-level crystal field model the corresponding gap was estimated for the different Si/Ge ratio samples, revealing that the crystal field splitting increases linearly with Si content.

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I. INTRODUCTION

Recent studies in the $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds with R = rare-earth elements reveal the existence of large magnetic effects leading to peculiar physical properties.^{1–3} In the past these materials did not receive much attention,⁴ until 1997 when Pecharsky and Gschneidner discovered the giant magnetocaloric effect (MCE) in $\text{Gd}_5\text{Si}_2\text{Ge}_2$,⁵ which stimulated intense research in many fundamental aspects in these exotic compounds. Associated with this giant MCE in $\text{Gd}_5\text{Si}_2\text{Ge}_2$, two more effects were promptly discovered: large magnetoresistance (MR) and giant magnetostriction (MS), which classified the compound as an extremum material.⁶ These impressive effects are induced by a spontaneous first-order structural transition (martensitic-like) from a monoclinic (M) to an orthorhombic Gd_5Si_4 [O(I)] phase, coupled to a paramagnetic (PM)–ferromagnetic (FM) transition.^{7–9} An important feature of this magnetostructural transition, namely for technological applications, is that it can be easily triggered by an applied magnetic field and/or an applied hydrostatic pressure.^{10–13} These captivating features are also present in other $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds (with different R), some of them leading to other fascinating effects.^{14–18} They are intimately related to the peculiar crystal structure of these compounds, having 36 atoms per unit cell but arranged in two-dimensional sequential rigid nanolayers. Interface bonds (Si,Ge) between successive rigid nanolayers regulate the establishment of the particular crystallographic phase, namely through the bond/break of such covalent Si(Ge)–Si(Ge) dimers.^{8,19,20}

Two different types of interaction play a role in this complex system: the intralayer magnetic interactions ruled by the

conventional 4f-4f Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect exchange²¹ and inducing FM order within each nanolayer, and the interlayer interactions arising from the spin polarization of the electrons in the Si(Ge) dimers, which tend to stabilize the FM phase (parallel magnetization in successive nanolayers). This spin polarization is caught and carried by the electrons in the p states of Ge(Si) element(s), which are strongly coupled to the spin polarization of the Gd $5d$ electron states^{21,22} and thus establish long-range RKKY interaction across the successive Gd-containing slabs.^{9,22} This interlayer coupling plays a central role toward the establishment of FM or AFM order (antiparallel magnetizations in successive nanolayers) in the compounds.

This polarization affects the electron energy states (and scattering) leading to an anomalous behavior in the electrical resistivity $\rho(T)$.^{23–25} We highlight that this type of measurement was a vital technique for the discovery of the training effect in these materials.^{24–26} Furthermore, an insulating-like behavior near the Néel temperature (T_N) was observed. This phenomenon was initially treated as a variational hopping mechanism²⁷ in the case of Gd_5Ge_4 , but more recently it was associated with the formation of an energy gap on the Fermi surface caused by the different magnetic and crystallographic periodicities.²⁶ Nevertheless, the physical origin of these effects is not clearly settled.

One main objective of the present work is to obtain a clear understanding of the intrinsic mechanisms and electronic states associated with each Si/Ge ratio and their dramatic effects in such different physical properties. Herein, we will discuss the influence of the Si/Ge ratio on the electronic structure of $\text{Ho}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds by studying $\rho(T)$.

Our previous studies, Refs. 28 and 29, reveal that the magnetic and crystallographic phase diagram is divided into three different regions: (i) For $x \leq 0.5$ one has an orthorhombic Sm_5Ge_4 [O(II)] structure (all the covalent bonds broken) in the whole temperature range (with exception of $x = 0$ ^{28,30}) with a magnetic transition from the PM to an AFM phase at low temperatures ($25 \text{ K} < T_N < 27 \text{ K}$). At low temperatures, these materials exhibit complex magnetic structures with the presence of some multiple commensurate states.²⁹ Furthermore, the sample with $x = 0$ presents first-order magnetostructural transitions changing from the O(II) to a $P2_1/m$ phase,^{28–30} and magnetically from the PM to the FM phase. (ii) For $x = 1$ one has an orthorhombic O(I) phase (all the covalent bonds formed) which supports (in decreasing T) a PM $\rightarrow$ FM transition at a Curie temperature $T_C \sim 75 \text{ K}$. (iii) In the intermediate region ($0.6 < x < 0.8$) the samples present a monoclinic (M) structure (half dimers bonded), leading to a FM state at low temperatures. Besides these (second-order) magnetic transitions of the disorder-order type, all compounds present another second-order transition (now order-order) at lower temperatures, producing a coherent rearrangement of the directions of the magnetic moment (a spin reorientation transition), which changes the magnetic propagation vector $\vec{K}$.²⁹

In agreement with the magnetic and crystallographic phase diagram, our $\rho(T)$ results confirm the three distinct behaviors, within the same diagram regions.

Concerning the FM materials, the experimental data reveal four distinct scattering mechanisms in $\rho(T)$: a residual term, a phonon term, a spin-dependent contribution, and further scattering due to the crystal field. For data analysis we used the Dekker model³¹ to treat the electron-spin collisions and the Grueneisen model for the phonon contribution, and assumed a two-level crystal field contribution. We found that the spin scattering gives the higher contribution to $\rho(T)$ in the FM phase, whereas the crystal field interactions lead to a characteristic curvature on $\rho(T)$ in the PM phase.

In the AFM materials $\rho(T)$ exhibits a large peak above T_N showing the presence of important precursor effects starting well above T_N . We use a phenomenological model to describe our experimental results and to obtain the amplitude of the different scattering components. The model contemplates the formation of an electronic superzone gap,^{31,32} as frequently observed in AFM materials below T_N (onset and subsequent growth of the gap).

II. EXPERIMENTAL DETAILS

Polycrystalline buttons of $\text{Ho}_5(\text{Si}_x\text{Ge}_{1-x})_4$ with $x = 0, 0.25, 0.5, 0.75, 0.875$, and 1 were synthesized by arc melting of stoichiometric mixtures of high-purity (99.99 wt %) Ho and high-purity (99.9999 wt %) Si and Ge. Further details about the sample preparation were given in Ref. 28. The six samples were cut from the initial ingots, having dimensions of $1.41 \times 1.21 \times 5.42 \text{ mm}^3$, $2.66 \times 0.97 \times 2.64 \text{ mm}^3$, $0.77 \times 1.51 \times 3.61 \text{ mm}^3$, $1.15 \times 1.21 \times 2.63 \text{ mm}^3$, $1.27 \times 1.16 \times 4.36 \text{ mm}^3$, and $1.39 \times 1.26 \times 3.44 \text{ mm}^3$ for $x = 0, 0.25, 0.5, 0.75, 0.875$, and 1 compounds, respectively. The electrical resistivity ρ was measured with the standard four-point potentiometric method using a dc current of 10 mA ,

stable to $1 : 10^6$. The voltage was measured with a Keithley 182 nanovoltmeter with resolution of 10 nV during the measurements. An automatic data acquisition system provided $R(T)$ data every second, in both temperature increase and decrease runs. These runs were made at a constant rate: $\partial T / \partial t = \pm 0.5 \text{ K/min}$, between $T = 10 \text{ K}$ and $T = 300 \text{ K}$.²⁴ Knowing the form factor ($f = \frac{S}{L}$; i.e., cross section/length ratio) of each sample one obtains $\rho(T) = f R(T)$. The thermopower and thermoconductivity measurements were performed using the differential method used in Ref. 33.

III. EXPERIMENTAL RESULTS

In this section we present the experimental results of the electrical resistivity [$\rho(T)$] in the range $10\text{--}300 \text{ K}$ for all six samples referred to in Sect. II. To simplify the analysis and interpretation of the results, we will group samples according to their particular magnetic phase and crystal structure within the above-mentioned temperature range.

A. Ho_5Si_4 : $x = 1$ [FM, O(I)]

Figure 1(a) displays the temperature dependence of the measured electrical resistivity [$\rho_{\text{exp}}(T)$] for the Ho_5Si_4 compound. It is observed that $\rho(T)$ exhibits a quasilinear temperature dependence (with a slight but extended negative curvature) above the critical temperature $T_C \sim 75 \text{ K}$, tending asymptotically to a strict linear behavior at high temperatures

FIG. 1. (Color online) (a) Temperature dependence of the measured (ρ_{exp}) electrical resistivity of Ho_5Si_4 in the temperature range $13\text{--}300 \text{ K}$ (black), and of the corresponding phonon and magnetic+crystal field components (blue and red, respectively). (b) Numerical derivative of the electrical resistivity of Ho_5Si_4 , neatly identifying T_C (PM-FM) and also T_{SR} but with less accuracy. This is associated with local defects in the crystal lattice which prevent smooth and fully coherent spin rotations. Notice the sharp and huge peak of $d\rho/dT$ at T_C (associated with the corresponding transition) and the effects of short-range spin fluctuations in the PM phase just above T_C and producing a small dip in $d\rho/dT$ (up to T^*).

TABLE I. Electrical resistivity values obtained from experimental data for $\text{Ho}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds.

Phase	x	Θ_D (K)	ρ_0 ($\mu\Omega \text{ cm}$)	α_{ph} ($\mu\Omega \text{ cm K}^{-1}$)	$\alpha_{\text{ph}}^{\text{norm}}$ (10^{-2})	$C_{\text{CF}}^{\text{norm}}$	δ (K)	$\rho_m^{\text{norm}}(\infty)$	Γ
O(II)/AFM	0	226.9	220.1	2.73			187.6		
	0.25	227.6	445.59	1.36	2.01	0.45	224.8	0.05	0.217
	0.5	228.4	3418.8	8.11	2.14	0.49	267.2	0.05	0.219
M/FM	0.75	229.3	483.3	4.60	1.19	0.37	273.0	0.46	
	0.875	229.8	85.0	1.27	1.27	0.32	281.2	0.46	
O(I)/FM	1	230.3	61.2	1.20	1.09	0.15	297.3	0.65	

(already established at 300 K). Such linear term arises from electron-phonon scattering whereas the small negative curvature, which precedes this behavior, is due to crystal field effects (saturating below room temperature). The slight upturn in the curve on the approach of T_C from above is attributed to critical spin-fluctuation effects. Just below T_C , a sudden decrease of ρ ($\Delta\rho \sim 60 \mu\Omega \text{ cm}$) is associated with the onset of the FM phase. This assumption is in accordance with linear thermal expansion (LTE) measurements in Ref. 28 where a change of the thermal expansion is observed at $T = T_C$. Lowering the temperature, the decrease of magnetic fluctuations in the FM phase strongly reduces the electron-spin scattering processes, and thus $\rho(T)$. Then a small change in the $\rho(T)$ behavior occurs at $T_{\text{SR}} \sim 17$ K, marking the onset of a coherent rearrangement of the magnetic moments through a second-order spin reorientation transition.²⁸ This transition is better displayed in the $d\rho/dT$ curve [Fig. 1(b)], where a change in the sign of the $d\rho/dT$ slope is observed near T_{SR} , like the one previously observed in $\text{Tb}_5\text{Si}_2\text{Ge}_2$.³⁴ This result

correlates well with previous magnetization and neutron data for Ho_5Si_4 ,^{28,29} giving $T_C = 77$ K and $T_{\text{SR}} = 15$ K. For future consideration, let us point out that the residual resistivity (ρ_0) of Ho_5Si_4 has a small value, $\rho_0 = 61.2 \mu\Omega \text{ cm}$ (Table I), due to the absence of (Si,Ge) mixing here.

Figure 1 also displays the different components of the electrical resistivity, which will be analyzed in Sec. IV.

B. Samples with $0.75 \leq x \leq 0.875$: [FM, M]

In these compounds with ferromagnetic phase and the monoclinic crystallographic structure [FM, M], $\rho(T)$ exhibits a behavior similar to that in the previous [FM, O(I)] compounds, as can be observed in Fig. 2 for the samples with $x = 0.75$ and 0.875 [Figs. 2(a.1) and 2(b.1), respectively].

The experimental data give $T_C \sim 50$ and 54 K and $T_{\text{SR}} \sim 18$ and 15 K for $x = 0.75$ and 0.875 , respectively [better observed in the numerical derivative $d\rho/dT$ shown in Figs. 2(a.2) and 2(b.2)]. One notices the modest increase of the residual

FIG. 2. (Color online) Temperature dependence of the measured electrical resistivity (ρ_{exp} ; black curves). (a.1) $\text{Ho}_5(\text{Si}_{0.75}\text{Ge}_{0.25})_4$ and (b.1) $\text{Ho}_5(\text{Si}_{0.875}\text{Ge}_{0.125})_4$ in the range 13–300 K; decomposed phonon and magnetic + crystal field components (blue and red, respectively). (a.2) and (b.2): Temperature dependence of $d\rho/dT$ for the same compounds. Inset (b.2): Thermal conductivity of $\text{Ho}_5(\text{Si}_{0.875}\text{Ge}_{0.125})_4$ in temperature range 10–100 K.

resistivity when one goes from Ho_5Si_4 ($\rho_0 = 61.2 \mu\Omega \text{ cm}$) to $x = 0.875$ ($\rho_0 = 85.0 \mu\Omega \text{ cm}$). This could simply reflect the effects of Si-Ge disordered mixing in the latter. However, for $x = 0.75$ a drastic increase occurs in the residual resistivity ($\rho_0 = 483 \mu\Omega \text{ cm}$). Usually, in metallic systems such values are only attained in the fully disordered amorphous state, implying an electron mean free path of the order of the interatomic distances. Some other mechanism(s) may be at work in this composition, drastically reducing the electronic conduction (see Sec. IV).

C. Samples with $x \leq 0.5$: [AFM, O(II)]

Figure 3 displays $\rho_{\text{exp}}(T)$ from 10 to 300 K for the compounds with Si concentration of $x = 0, 0.25$, and 0.5 , which exhibit an [AFM, O(II)] phase at low temperatures and a [PM, O(II)] phase above T_N .

In the PM phase, all the samples present a linear $\rho(T)$ dependence well above T_N ($T > 6T_N$), characteristic of electron-phonon scattering. On cooling from this regime, a small negative curvature sets in $\rho(T)$, followed at lower temperatures by a neat upturn in $\rho(T)$, precursor of the PM $\rightarrow$ AFM transition at the Néel temperature. Physically, T_N occurs at the inflection point in $\rho(T)$, giving $T_N \sim 30, 32$, and 35 K for $x = 0, 0.25$, and 0.5 , respectively. Then $\rho(T)$ peaks at a maximum slightly below T_N (ρ_{max} at T_{max}). The origin of these features will be further discussed in Sec. IV.

In the case of Ho_5Ge_4 [Fig. 3(a)], one should notice the abrupt decrease of $\rho(T)$ at $T = T_S$ just below T_{max} , representing a variation of $\Delta\rho \sim 230 \mu\Omega \text{ cm}$. The origin of this discontinuity stems from a first-order O(II) $\rightarrow$ M structural transition, leading to a new monoclinic phase ($P2_1/m$), as recently revealed by neutron scattering measurements.^{29,30} At still lower temperature another resistivity anomaly marks the onset of a spin reorientation transition, at $T_{\text{SR}} = 18$ K. In the other cases ($x = 0.25$ and 0.5) the first-order character of the transition just below T_{max} disappears, indicating the absence of a structural transition. The continuous (but significant) decrease of ρ below T_{max} is then attributed to the increase of the spontaneous magnetic order, which reduces electron spin scattering. Again, at lower temperatures a spin reorientation appears, at $T_{\text{SR}} \sim 15$ K in both cases.

FIG. 3. (Color online) Temperature dependence of the electrical resistivity for compounds of $\text{Ho}_5(\text{Si}_x\text{Ge}_{1-x})_4$ with $x = 0, 0.25$, and 0.5 . Insets: (b) Temperature dependence of thermal conductivity in range 10–100 K; (c) scanning electron microscopic image showing the presence of considerable microcracks in the $x = 0.5$ compound.

FIG. 4. (Color online) Normalized $\rho(T)$ for compounds of $\text{Ho}_5(\text{Si}_x\text{Ge}_{1-x})_4$ with $x = 0.25, 0.5, 0.75, 0.825$, and 1 , with the temperature limits of 298 K and 13 K. Inset: Residual electrical resistivity as a function of Si concentration.

IV. DISCUSSION

The results in the last section show that $\rho(T)$ strongly depends on the relative Si/Ge concentration. This is better observed in the normalized resistivity $\rho_n(T) = \frac{\rho(T) - \rho(298 \text{ K})}{\rho(298 \text{ K}) - \rho(13 \text{ K})}$ shown in Fig. 4. This plot enables us to compare the relative $\rho(T)$ variations in different samples and structures, without the uncertainties of the sample form factor and the residual resistivity. It is well known that in these materials the form factor and the residual resistivity can be rather complex, due to the peculiar microstructure presented, including open/closed site bonds, defects, internal strain fields, and microcrack contributions. They explain the unusual behavior of ρ_0 along the series (x from 0 to 1), as shown in the inset of Fig. 4. In particular, the value $\rho_0 = 3418.8 \mu\Omega \text{ cm}$ (apparent) for $x = 0.5$ seems incompatible with the metallic behavior exhibited by the corresponding $\rho(T)$ curve. Such discrepancy is likely due to intense internal cracking, which greatly affects the effective form factor of the sample. This is consistent with the SEM picture [inset of Fig. 3(c)], where large microcracks appear at this particular composition. After removing these contributions by the above normalization, one obtains an excellent overlap of the electrical resistivity curves belonging to compounds with the same lattice and magnetic structure,

which are the ruling parameters on the $\rho(T)$ behavior, as discussed below.

The referred normalization is then quite appropriate to compare the $\rho(T)$ behavior in the different compounds of our system, where $\rho(T)$ presents several anomalies.²⁴ The only exception is the case of the residual resistivity, which obviously is eliminated in such normalization.

A. FM compounds ($x > 0.5$)

In general, $\rho(T)$ for simple FM R-based compounds presents four independent electron scattering mechanisms: the electrostatic potential associated with permanent lattice irregularities (point defects, impurities, microcracks, etc.) leading to the residual resistivity (ρ_0), the phonon scattering (ρ_{ph}) arising from the atomic vibrations, and the spin-dependent scattering (ρ_m) of the conduction electrons with ionic (R³⁺) localized magnetic moments. In addition, there is the crystal field effect which arises from the perturbation of the electrostatic field of each magnetic ion by the nearby ions. This surrounding leads to a splitting of the initial (isolated ion) degenerate energy states, thus changing the ion cross section for collision with a conduction electron. This contribution (ρ_{CF}) is larger in rare earth elements which present a pronounced charge anisotropy of the incomplete 4f shell, as occurs with Ho³⁺. Concerning the above scattering processes, the total electrical resistivity (ρ_t) is usually well accounted for by the sum of the different contributions (Matthiessen's rule):

$$\rho_t(T) = \rho_0 + \rho_{ph}(T) + \rho_m(T) + \rho_{CF}(T). \quad (1)$$

The lattice vibration contribution $\rho_{ph}(T)$ usually follows the Bloch-Grüneisen law:³⁵

$$\rho_{ph}(T) = 4\alpha_{ph}\Theta_D \left(\frac{T}{\Theta_D}\right)^5 \int_0^{\frac{\Theta_D}{T}} \frac{x^5}{(e^x - 1)(1 - e^{-x})} dx. \quad (2)$$

In the high-temperature limit ($T > \Theta_D$, Debye temperature) the Debye model Eq. (2) gives $\rho_{ph}(T) = \alpha_{ph}T$, where α_{ph} is a constant for each compound (or electron-phonon coupling). At low temperatures, the Debye model gives a cubic dependence of $\rho(T)$. Nevertheless, it does not accurately predict where this transition occurs. From numerical simulations, we observe an almost linear regime around $\frac{\Theta_D}{3}$. Considering the slope of the linear part of $\rho(T)$ at high temperatures and estimating Θ_D from the chemical stoichiometry and the molar masses at play,

$$\Theta_D = \frac{5\Theta_D^{\text{Ho}} M_{\text{Ho}} + 4x\Theta_D^{\text{Si}} M_{\text{Si}} + (4 - 4x)\Theta_D^{\text{Ge}} M_{\text{Ge}}}{M_{\text{mol}}}, \quad (3)$$

where M is the molecular mass (see Table I), and we used $\Theta_D^{\text{Ho}} = 175$ K, $\Theta_D^{\text{Si}} = 636$ K, and $\Theta_D^{\text{Ge}} = 374$ K from Ref. 36. From this calculation it is straightforward to obtain the $\rho_{ph}(T)$ contribution as depicted in Figs. 1 and 2. The residual value ρ_0 was obtained from the $\rho(T)$ extrapolation to $T = 0$ K. Using Eqs. (1) and (2) one then extracts the $\rho_m + \rho_{CF}$ components of $\rho_t(T)$, as depicted in Figs. 1(a), 2(a.1), and 2(b.1) for the different FM compounds. Since the magnetic contribution for temperatures sufficiently above T_C should be virtually constant [$\rho_m(\infty)$; PM phase], the evident negative curvature observed in $\rho(T)$ in the PM phase is related to the crystal field effect.

Due to the complexity of determining the exact Ho electronic level schemes in this system (Ho occupies three different crystal sites), the single-spacing (δ) crystal field model was adopted to estimate the order of magnitude of the crystal field splitting.³⁷ The adequacy of such model was tested through a fit of the electrical resistivity data, involving the following model equation for $\rho_{CF}(T)$:³⁷

$$\rho_{CF}(T) = \frac{C_{CF}}{\cosh^2\left(\frac{\delta}{2k_B T}\right)}, \quad (4)$$

where C_{CF} is the crystal field quantity component and k_B is the Boltzmann constant. Since the crystal field effects extend well above T_C , we fitted the resistivity in this phase with the expression $\rho(T) = B + \alpha_{ph}T + \frac{C_{CF}}{\cosh^2\left(\frac{\delta}{2k_B T}\right)}$, where $B = \rho_m(\infty) + \rho_0$. The values obtained from the fit of the normalized curves are given in Table I, and indeed one sees that the single-spacing (δ) CF model leads to a good fit of the $\rho(T)$ data over the whole PM range.

To extend the description of $\rho(T)$ below T_C , one uses $\rho_m(T)$ given by the Dekker model,^{31,38} restricted to elastic electron scattering and to a mean field approximation (MFA) for the magnetic structure:

$$\frac{\rho_m(T)}{\rho_m(\infty)} = \left[1 - \frac{\langle J_z \rangle^2}{J(J+1)} - \frac{\langle J_z \rangle}{J(J+1)} \tanh\left(\frac{3T_C \langle J_z \rangle}{2T(J+1)}\right) \right], \quad (5)$$

where $\rho_m(\infty) = \frac{3\pi m^* J(J+1) \mathcal{J}_s^2}{2e^2 \hbar E_F}$, the so-called De Gennes constant, J is the total magnetic moment, $\mathcal{J}_s$ is the scattering factor between the electron and the magnetic moment, m^* is the effective mass, e is the electron charge, $\hbar$ is the reduced Planck constant, E_F is the Fermi energy, and $\langle J_z \rangle$ is the spontaneous magnetization expressed by $J B_J(x)$, where $B_J(x)$ is the Brillouin function of index J .

Using the values of Table I, the critical temperature $T_C = 50$ K, the total Ho³⁺ ion angular momentum ($J = 8$), and Eqs. (1)–(5) after using the respective conversion factor [i.e., multiplying the experimental values of $[\rho(13) - \rho(298)]$ and summing the value of $\rho(298)$], we numerically simulate the $\rho(T)$ dependence from 13 to 300 K, obtaining the result displayed in Fig. 5 for Ho₅(Si_{0.75}Ge_{0.25})₄. Fairly good accordance is obtained between experimental and numerical results, except for some small differences at low temperatures near the spin reorientation transition, which is not considered in the above model. Furthermore, for temperatures below $T < T_{SR}$, $d\rho/dT$ presents a linear temperature dependence extrapolating to $d\rho/dT = 0$ at absolute zero [see Fig. 1(b), Fig. 2(a.2), and Fig. 2(b.2)], revealing that $\rho(T)$ scattering is dominated by electron magnon scattering, leading to a quadratic T dependence of $\rho(T)$ in this region. A similar and successful numerical simulation was also performed for the Ho₅(Si_{0.875}Ge_{0.125})₄ compound.

B. Superzone-gap-like AFM compounds ($x \leq 0.5$)

These samples are AFM at low temperatures, so the $\rho(T)$ magnetic contribution cannot be described by the previous Dekker model. In rare-earth AFM elements, one knows that $\rho(T)$ increases over a significant range of temperature below T_N , with a negative curvature, due to the formation at T_N of a superzone gap near the Fermi level, which

FIG. 5. (Color online) Comparison the $\rho(T)$ experimental data and its numerical simulation considering Eqs. (1)–(3) and the values in Table I for $\text{Ho}_5(\text{Si}_{0.75}\text{Ge}_{0.25})_4$, in the 13–300 K range.

increase as T decreases.^{31,39} This gap is proportional to the staggered spontaneous magnetization, reducing the number of effective conduction electrons and thus increasing ρ below T_N .^{31,39} Physically, this gap results from the new periodicity (AFM) below T_N , besides the crystallographic one. The effect resembles some features observed in the present case (Fig. 3). However, we notice that $\rho(T)$ starts increasing (on cooling) well above T_N [$\sim 1.7T_N$; see $d\rho/dT$, Fig. 6(a)] and with a positive curvature in ρ (Fig. 7), which is not expected. This indicates the early onset of important precursor effects in the PM phase on the approach to T_N . These effects are of magnetic origin, as evidenced by the analysis of previous magnetic data obtained in these samples.²⁸ In fact, the reciprocal susceptibility [χ^{-1} ; see Fig. 6(b)] clearly departs from the traditional Curie-Weiss law in the paramagnetic phase at $T = T_G = 74$ K, well above $T_N = 31$ K. This behavior proves the early existence of magnetic clusters in the PM phase, forming the so-called Griffiths-like phase, previously observed in $\text{Tb}_5\text{Si}_2\text{Ge}_2$, Gd_5Ge_4 in the $\text{Ho}_5(\text{Si}_{0.875}\text{Ge}_{0.125})_4$ compound.^{14,40,41} The presence of this phase was very recently extended to all the compounds presenting the M or O(II) crystallographic phases and in the $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system with $\text{R} = \text{Gd}, \text{Tb}, \text{Dy}$, and Ho .⁴² These magnetic clusters also give rise to a change in the thermopower $S(T)$ behavior below T_G [see Fig. 6(c)], with a departure from the expected $S \propto T$ dependence in the PM phase (Mott model) between T_G and T_N . On the other hand, a detailed analysis of the $S(T)$ data shows the presence of a small gaplike behavior near T_N .^{43–46}

Concerning the previous features, we extracted a magnetic order parameter by subtracting from 300 K until T_N the obtained arguments from the Curie-Weiss law ($\chi = \frac{C}{(T-\theta_p)}$), well above T_G , to the experimental susceptibility (Ref. 28), obtaining an appropriate magnetic order parameter, $\sigma = (\frac{\sigma_{\text{exp}}}{\sigma_{\text{max}}})$ [$\sigma_{\text{exp}} = \frac{M(T,H)}{H} - \frac{C}{(T-\theta_p)}$] [see Fig. 6(d)], where it can be observed that below T_G an increase of σ is observed arising from the magnetic clusters. We use such σ parameter and the crystal field component in the usual equation to account for the effect of the superzone gap on $\rho(T)$ (the gap effect appears only in the denominator^{31,39}), both below and above T_N :

$$\rho(T) = \frac{\rho_0 + \alpha_{\text{ph}}T + \frac{C_{\text{CF}}}{\cosh^2(\frac{\epsilon}{2kT})} + \rho_m(\infty)(1 - \frac{1}{2}\sigma^2)}{1 - \Gamma \frac{\sqrt{5}}{3}\sigma}, \quad (6)$$

FIG. 6. (Color online) Experimental results for $\text{Ho}_5(\text{Si}_{0.5}\text{Ge}_{0.5})_4$ near T_N . (a) Numerical $d\rho/dT$. (b) Reciprocal susceptibility (χ^{-1}). (c) Thermopower $S(T)$. (d) Scaled magnetic order parameter ($\sigma/\sigma_{\text{max}}$).

where Γ is related with the supergap zone. Equation (6) fits all the $\rho(T)$ curves of our AFM compounds, with exception of Ho_5Ge_4 due its first-order magnetostructural transition.

Figure 7 depicts the performed fit for the concentration $x = 0.5$, giving a total overlap with the experimental data in the whole temperature range 13–300 K. Similar results were obtained for the sample with $x = 0.25$ (not shown).

The good agreement between the experimental data and the model reveals that the effect of the superzone gap exists below and above T_N , and is well accounted by Eq. (6) and concerning the order parameter σ .^{31,39} It seems that the superzone gap above T_N is due to the formation of magnetic clusters in the PM phase. Such clusters have been pointed out to come from the strong competition between the intralayer FM interactions and the interlayer AFM interactions that are present in the O(II) phase.²¹ Nevertheless the real nature of these magnetic clusters (and the superzone gap effect above T_N) is still being pursued.

The formation of a superzone gap was also invoked to explain the $\rho(T)$ behavior of $\text{Dy}_{0.5}\text{Gd}_{4.5}\text{Si}_2\text{Ge}_2$ below T_N .²⁶

FIG. 7. (Color online) Temperature dependence of $\rho(T)$ for $\text{Ho}_5(\text{Si}_{0.5}\text{Ge}_{0.5})_4$ in the range 13–300 K (black line) and the fitted results using Eq. (6) (green line). Inset: Crystal field splitting as a function of Si concentration.

We highlight that here the superzone gap appears when the system changes from the FM to the AFM state on cooling, following the usual behavior of the simple rare-earth metals.^{31,32,39}

In the particular case of Ho_5Ge_4 , the $\rho(T)$ data was only fitted in the PM phase above T_N , $\rho(T) = \rho_0 + \rho_m(\infty) + \alpha_{\text{ph}}T + \frac{C_{\text{CF}}}{\cosh^2(\frac{\delta}{2kT})}$, due to the complication introduced by the magnetostructural transition just below T_N .

The above fits were done for all the AFM samples, as a control of the values obtained for the different parameters. Table I summarizes the results obtained from the normalized curves in the studied AFM materials, where it can be observed that Γ is smaller than the theoretical value obtained by Elliot *et al.*³⁹ ($\Gamma = 0.58$ for Ho), revealing a gap with much lower magnitude in the present compounds. Nevertheless, we cannot rule out the strong chemical disorder induced localization, within the interslab regions (Si/Ge) on the approach of the magnetic phase transitions, becoming maximum at the transition point [critical fluctuations giving an inflexion point in the $\rho(T)$ curve]. We also notice that random (Si,Ge) impurities in the samples in the range $0.25 \leq x \leq 0.825$, besides a dominant contribution in ρ_0 , also lead to a dominant electron-impurity scattering behavior of the thermal conductivity ($K = \text{const. } T$) at low temperatures, as displayed in the insets of Fig. 2(b,2) and Fig. 3(b).

C. Overview of the analysis results

One should notice the striking differences in the $\rho(T)$ behavior near the PM-FM (T_C) and near the PM-AFM (T_N) transitions. As T decreases toward the FM critical point, $\rho(T)$ only shows a slight upturn arising from the critical enhancement of the spin fluctuations, followed by a sudden decrease of $\rho(T)$ (at $T < T_C$) due to the onset and subsequent increase of the long-range spontaneous magnetic order. In the case of $x = 1$, an additional contribution arises from a volume change, previously observed in linear thermal expansion measurements.²⁸ This contrasts with the AFM samples where important magnetic clustering occurs for $T_N < T \lesssim 2T_N$, leading to a decrease of the number of electron carriers near the Fermi level, and thus to an increase of ρ as T decreases toward T_N , due to the opening of the superzone gap. This is an interesting clustering effect which deserves further investigation (in progress). In particular, a superzone gap requires sizable clusters (to display such electron-band features), namely being larger than the electron mean free path and the Fermi wavelength.

In the inset of Fig. 7 one sees the observed linear dependence of the crystal field split parameter (δ) on Si concentration (x), over the whole Si range. Looking at Table I, one sees that the crystal field parameter C_{CF} depends on the crystallographic structure, presenting higher magnitude on the O(II) structure. The phonon contribution $\alpha_{\text{ph}}^{\text{norm}}$ is higher in the O(II) phase than in the O(I) phase, as one should expect since Ge has a much higher mass than Si. One notices that the α_{ph} values obtained are of the same order as those measured in the Tb compounds, $\alpha_{\text{ph}} = 5.7 \mu\Omega \text{ cm K}^{-1}$,³⁴ but are an order of magnitude higher than in a Ho polycrystal metal.³² The $\rho_m(\infty)$ values reveal that the space group symmetry plays an important role in the $\rho(T)$ behavior, with the O(I) crystallographic structure producing

the higher magnetic contribution (see Fig. 4). It is noteworthy that $\rho_m(\infty)$ increases with the relative increase of Si in the case of FM materials (see Table I), indicating an increase of the $\frac{m^* \mathcal{J}_{\text{sl}}^2}{E_F}$ ratio. Microscopically, with the increase of Si, it is expected that there will be reforming of covalent Si(Ge)-Si(Ge) bonds across the interslab space, which raises the magnetic exchange interaction between nearby slabs through the spin polarization of the dimer.²² This can be an important obstacle for charge conduction by the free electrons. Furthermore, one recalls that the increase of the Si content decreases the unit cell volume and so the interatomic distance (such as a pressure effect^{9,11}), leading to an increase of the magnetic scattering between the conduction electrons and the R^{3+} ions and/or to a change in the Fermi surface.

V. CONCLUSIONS

We have carried out a detailed study of $\rho(T)$ for $\text{Ho}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds covering all the different regions of the phase diagram. Our results reveal that in the FM materials the $\rho(T)$ behavior is mainly dominated by the electron-spin scattering mechanism with an additional crystal field component. This crystal field plays an important role in all materials in the PM phase, inducing a characteristic curvature in $\rho(T)$. Our analysis shows a linear dependence of the crystal field gap split δ with the Si amount. It is also suggested (using a phenomenological model) that the “insulating-like” effect observed near T_N arises from the spontaneous onset of the magnetic periodicity in the vicinity of the percolation temperature, leading to a decrease of the conduction electron concentration and thus to an increase of $\rho(T)$. These effects extend to temperatures well above T_N due the presence of short-range magnetic clusters in the PM phase (internally exhibiting AFM-like order) that seem to arise from the strong competition between the intra- and interslab interactions. Furthermore, our results reveal the existence of a complex microstructure inside the samples (internal strain, microcracks, point defects, etc.), leading to an unusual residual resistivity or shape factor variation with Si/Ge ratio. Finally, this work elucidates the strong coupling between the magnetic and atomic structures, namely the corresponding effect on the electronic structure when the x (Si/Ge) ratio is changing along the complete $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$ series. New experiments and more extended research are still needed to clarify the issues raised in this work. For example, to directly obtain the crystal field parameters, inelastic neutron scattering on single crystals is needed, complemented with other transport property studies such as thermal conductivity, thermopower, and the Hall effect. Some of these studies are still in progress and are beyond the scope of the present paper.

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- ¹K. A. Gschneidner Jr., V. K. Pecharsky, and A. O. Tsokol, *Rep. Prog. Phys.* **68**, 1479 (2005).
- ²G. J. Miller, *Chem. Soc. Rev.* **35**, 799 (2006).
- ³A. O. Pecharsky, K. A. Gschneidner Jr., V. K. Pecharsky, D. L. Schlagel, and T. A. Lograsso, *Phys. Rev. B* **70**, 144419 (2004).
- ⁴F. Holtzberg, R. J. Gambino, and T. R. McGuire, *J. Phys. Chem. Solids* **28**, 2283 (1967).
- ⁵V. K. Pecharsky and K. A. Gschneidner Jr., *Phys. Rev. Lett.* **78**, 4494 (1997).
- ⁶V. K. Pecharsky and K. A. Gschneidner Jr., *Adv. Mater.* **13**, 683 (2001).
- ⁷V. K. Pecharsky and K. A. Gschneidner Jr., *J. Alloys Compd.* **260**, 98 (1997).
- ⁸W. Choe, A. O. Pecharsky, M. Worle, and G. J. Miller, *Inorg. Chem.* **42**, 8223 (2003).
- ⁹V. K. Pecharsky, G. D. Samolyuk, V. P. Antropov, A. O. Pecharsky, and K. A. Gschneidner Jr., *J. Solid State Chem.* **171**, 57 (2003).
- ¹⁰L. Morellon, P. A. Algarabel, M. R. Ibarra, J. Blasco, B. Garcia-Landa, Z. Arnold, and F. Albertini, *Phys. Rev. B* **58**, R14721 (1998).
- ¹¹C. Magen, L. Morellon, P. A. Algarabel, M. R. Ibarra, Z. Arnold, and C. Ritter, *Adv. Solid State Phys.* **46**, 241 (2007).
- ¹²L. Morellon, Z. Arnold, P. A. Algarabel, C. Magen, M. R. Ibarra, and Y. Skorokhod, *J. Phys. Condens. Matter* **16**, 1623 (2004).
- ¹³C. Magen, Z. Arnold, L. Morellon, Y. Skorokhod, P. A. Algarabel, M. R. Ibarra, and J. Kamarad, *Phys. Rev. Lett.* **91**, 207202 (2003).
- ¹⁴C. Magen, P. A. Algarabel, L. Morellon, J. P. Araujo, C. Ritter, M. R. Ibarra, A. M. Pereira, and J. B. Sousa, *Phys. Rev. Lett.* **96**, 167201 (2006).
- ¹⁵E. M. Levin, V. K. Pecharsky, and K. A. Gschneidner Jr., *Phys. Rev. B* **63**, 174110 (2001).
- ¹⁶M. Zou, H. Tang, D. L. Schlagel, T. A. Lograsso, K. A. Gschneidner, and V. K. Pecharsky, *J. Appl. Phys.* **99**, 08B304 (2006).
- ¹⁷S. B. Roy, M. K. Chattopadhyay, P. Chaddah, J. D. Moore, G. K. Perkins, L. F. Cohen, K. A. Gschneidner Jr., and V. K. Pecharsky, *Phys. Rev. B* **74**, 012403 (2006).
- ¹⁸N. K. Singh, V. K. Pecharsky, and K. A. Gschneidner Jr., *Phys. Rev. B* **77**, 054414 (2008).
- ¹⁹C. Magen, L. Morellon, P. A. Algarabel, M. R. Ibarra, Z. Arnold, J. Kamarad, T. A. Lograsso, D. L. Schlagel, V. K. Pecharsky, A. O. Tsokol, and K. A. Gschneidner Jr., *Phys. Rev. B* **72**, 024416 (2005).
- ²⁰L. Morellon, Z. Arnold, C. Magen, C. Ritter, O. Prokhnenko, Y. Skorokhod, P. A. Algarabel, M. R. Ibarra, and J. Kamarad, *Phys. Rev. Lett.* **93**, 137201 (2004).
- ²¹D. Paudyal, V. K. Pecharsky, and K. A. Gschneidner Jr., *J. Phys. Condens. Matter* **20**, 235235 (2008).
- ²²D. Haskel, Y. B. Lee, B. N. Harmon, Z. Islam, J. C. Lang, G. Srajer, Y. Mudryk, K. A. Gschneidner, and V. K. Pecharsky, *Phys. Rev. Lett.* **98**, 247205 (2007).
- ²³E. M. Levin, A. O. Pecharsky, V. K. Pecharsky, and K. A. Gschneidner Jr., *Phys. Rev. B* **63**, 064426 (2001).
- ²⁴J. B. Sousa, A. M. Pereira, F. C. Correia, J. M. Teixeira, J. P. Araujo, R. P. Pinto, M. E. Braga, L. Morellon, P. A. Algarabel, C. Magen, and M. R. Ibarra, *J. Phys. Condens. Matter* **17**, 2461 (2005).
- ²⁵J. B. Sousa, M. E. Braga, F. C. Correia, F. Carpinteiro, L. Morellon, P. A. Algarabel, and M. R. Ibarra, *Phys. Rev. B* **67**, 134416 (2003).
- ²⁶R. Nirmala, V. Sankaranarayanan, K. Sethupathi, A. V. Morozkin, Y. Yamamoto, and H. Hori, *Physica B* **373**, 120 (2006).
- ²⁷E. M. Levin, V. K. Pecharsky, K. A. Gschneidner Jr., and G. J. Miller, *Phys. Rev. B* **64**, 235103 (2001).
- ²⁸A. M. Pereira, J. B. Sousa, J. P. Araujo, C. Magen, P. A. Algarabel, L. Morellon, C. Marquina, and M. R. Ibarra, *Phys. Rev. B* **77**, 134404 (2008).
- ²⁹C. Ritter, C. Magen, L. Morellon, P. A. Algarabel, M. R. Ibarra, A. M. Pereira, J. P. Araujo, and J. B. Sousa, *Phys. Rev. B* **80**, 104427 (2009).
- ³⁰N. K. Singh, D. Paudyal, Y. Mudryk, V. K. Pecharsky, and K. A. Gschneidner Jr., *Phys. Rev. B* **79**, 094115 (2009).
- ³¹B. Coqblin, *The Electronic Structure of Rare-Earth Metals and Alloys: The Magnetic Heavy Rare-Earths* (Academic Press, Inc., New York, 1977).
- ³²R. Elliott, *Magnetic Properties of Rare Earth Metals* (Plenum Press, London and New York, 1972).
- ³³J. B. Sousa, R. P. Pinto, M. M. Amado, M. E. Braga, and Junji Sakurai, *J. Magn. Magn. Mater.* **28**, 29 (1982).
- ³⁴J. P. Araujo, A. M. Pereira, M. E. Braga, R. P. Pinto, J. M. Teixeira, F. C. Correia, J. B. Sousa, L. Morellon, P. A. Algarabel, C. Magen, and M. R. Ibarra, *J. Phys. Condens. Matter* **17**, 4941 (2005).
- ³⁵N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958).
- ³⁶D. R. Lide, *Handbook of Chemistry and Physics* (CRC Press, Boca Raton, 2001-2002).
- ³⁷K. Hiebl and O. Sologub, *J. Magn. Magn. Mater.* **186**, 56 (1998).
- ³⁸J. M. Moreira, Ph.D. thesis, Porto University, 1985.
- ³⁹R. J. Elliott and F. A. Wedgwood, *Proc. Phys. Soc. London* **81**, 846 (1963).
- ⁴⁰Z. W. Ouyang, V. K. Pecharsky, K. A. Gschneidner Jr., D. L. Schlagel, and T. A. Lograsso, *Phys. Rev. B* **74**, 094404 (2006).
- ⁴¹N. K. Singh, D. Paudyal, Y. Mudryk, V. K. Pecharsky, and K. A. Gschneidner, *Phys. Rev. B* **81**, 184414 (2010).
- ⁴²A. M. Pereira, L. Morellon, C. Magen, J. Ventura, P. A. Algarabel, M. R. Ibarra, J. B. Sousa, and J. P. Araujo, *Phys. Rev. B* **82**, 172406 (2010).
- ⁴³A. M. Pereira, J. P. Araujo, M. E. Braga, R. P. Pinto, J. Ventura, F. C. Correia, J. M. Teixeira, J. B. Sousa, C. Magen, P. A. Algarabel, L. Morellon, M. R. Ibarra, and J. B. Sousa, *J. Alloys Compd.* **423**, 66 (2006).
- ⁴⁴A. M. Pereira, C. Magen, J. P. Araujo, P. A. Algarabel, L. Morellon, M. E. Braga, R. P. Pinto, M. R. Ibarra, and J. B. Sousa, *J. Magn. Magn. Mater.* **310**, e580 (2007).
- ⁴⁵A. M. Pereira, C. Magen, M. E. Braga, R. P. Pinto, R. Fermento, P. A. Algarabel, L. Morellon, M. R. Ibarra, J. P. Araujo, and J. B. Sousa, *J. Non-Cryst. Solids* **354**, 5298 (2008).
- ⁴⁶R. P. Pinto, J. B. Sousa, F. C. Correia, J. P. Araujo, M. E. Braga, A. M. Pereira, L. Morellon, P. A. Algarabel, C. Magen, and M. R. Ibarra, *J. Magn. Magn. Mater.* **290-291**, 661 (2005).