Electron spin resonance and magnetic characterization of the $Gd_{5.09}Ge_{2.03}Si_{1.88}$

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Electron spin resonance was applied on samples of $Gd_{5.09}Ge_{2.03}Si_{1.88}$. The results are discussed under the scope of magnetization measurements, optical metallography, and wavelength dispersive spectroscopy. Polycrystalline arc-melted samples submitted to different heat treatments were investigated. The correlation of the electron spin resonance and magnetization results permitted a characterization of the present phases and their transitions. Two coexisting phases in the temperature range between two phase transitions have been identified and associated to distinct crystallographic phases. Additionally, the magnetic moment at high temperatures has been estimated from the measured effective *g* factor. A peak value of 21.5 J/kg K for the magnetocaloric effect was obtained for a sample heat treated at 1500 °C for 16 h.

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INTRODUCTION

The conjunction of several characteristics of the compound $Gd_{5.09}Ge_{2.03}Si_{1.88}$, which lead to the magnetic and crystallographic transitions related to the observed giant magnetocaloric effect (GMCE), opened a wide range of specific studies about these characteristics. It has been shown, for instance, that the paramagnetic (PM) and ferromagnetic (FM) phases coexist around the transition temperature and also that there is a reversibility of the transitions in relation to changes of applied magnetic field and temperature.[1–3] Furthermore, the way by which the preparation and heat treatment of the samples affects the GMCE has been investigated in detail.[2,4,5] In order to interpret experimental data for the $Gd_5(Ge_{1-x}Si_x)_4$ family, different possibilities of magnetic ordering are taken into account. Distinct FM and even antiferromagnetic arrangements were already considered.[2,6,7]

In this work we present experimental results on electron spin resonance (ESR) measurements on the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ compound as a function of temperature. This alloy has the stoichiometry of the majority phase of the $Gd_5Ge_2Si_2$ alloy as determined by wavelength dispersive spectroscopy (WDS).[5] The association of the observed ESR lines with such majority phase and an additional one is done, leading to the study of their individual magnetic behavior. The magnetic moment at high temperatures is derived and the ESR linewidth behavior is discussed. The same ESR analysis is applied to an as-cast sample and to a heat-treated one.

EXPERIMENTAL

The sample with the nominal composition $Gd_{5.09}Ge_{2.03}Si_{1.88}$ was prepared by arc melting the mixtures of 99.9 wt % Gd and electronic grade Ge and Si in an Ar atmosphere. ESR experiments were carried out for the as-cast sample and for another piece of the same sample submitted to a heat treatment also in Ar atmosphere at 1500 °C for 16 h. Magnetization measurements as a function of temperature (4 K to 350 K) and applied field (0 to 50 kOe) as well as optical metallography analysis were used as previous characterization. The heat-treated sample presented smaller hysteresis in the $M \times T$ cycle than the as-cast one (for an applied field of 200 Oe). The peak of the magnetocaloric effect (MCE) for the as-cast sample has a value of 14.5 J/kg K, smaller than the value for the similar compound $Gd_5Ge_2Si_2$ (e.g., Refs. 1–7), occurring approximately at the same temperature (~266 K). The $Gd_{5.09}Ge_{2.03}Si_{1.88}$ sample heat-treated at 1300 °C for 1 h, which is not the best heat treatment conditions for this alloy, has its MCE almost not changed (peak up to 15 J/kg K). The sample heat treated at 1500 °C for 16 h, studied in the present work, has a MCE peak value even larger (21.5 J/kg K) at around 270 K (Fig. 1).

The ESR measurements were carried out on a commercial VARIAN E-15 spectrometer operating at 9.3 GHz at temperatures between 205 K and 405 K. The series of spectra were obtained always heating the sample. The temperature in the resonance cavity was controlled by N_2 gas flux and the uncertainty in the determination of the sample temperature was smaller than 1 K. A dc-magnetic field from 0 to 10 kOe at a rate of 5 kOe/min and a modulation field with amplitude of 25 Oe at 100 kHz were employed. The results discussed here were obtained from polycrystalline plates extracted

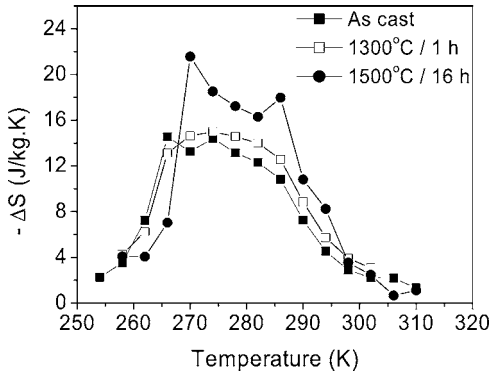

FIG. 1. Magnetic entropy change as a function of temperature for three $Gd_{5.09}Ge_{2.03}Si_{1.88}$ samples for a magnetic field change of 50 kOe.

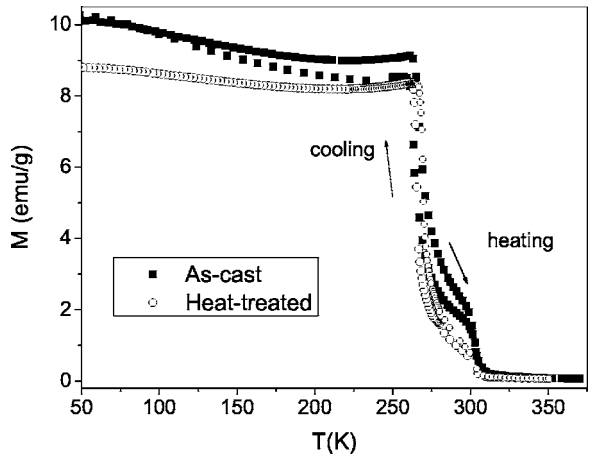

FIG. 2. Magnetization curves as a function of temperature (200 Oe). The values in both ordered regions are greater for the as-cast sample.

from the as-cast sample and from the one heat-treated at 1500 °C for 16 h. The shape of the samples is irregular with the approximate dimensions $3\times3\times1$ mm^3.

RESULTS AND ANALYSIS

Figure 2 shows low applied field magnetization curves for three main temperature regions. In the $T>302$ K high-temperature region, magnetization has only paramagnetic contributions. The intermediate region, 302 K$>T>$268 K, is delimited by two magnetic phase transitions, a second-order transition around 302 K and a first-order one around 268 K. Besides a larger heating-cooling hysteresis, the as-cast sample shows an ordered contribution in this intermediate region larger than the heat-treated sample. Although suitable preparation and heat treatment can practically eliminate such ordered magnetic phase,[4] its presence is usual when preparing the 5:2:2 compounds[5–7] and is often attributed to the coexistence of an orthorhombic modification of the 5:2:2 phase with the main monoclinic phase, as observed in sintered tablets of this compound.[8] Therefore, in this intermediate temperature range, one can affirm that the magnetization curve comprises two contributions. The first one is a paramagnetic contribution coming from the majority monoclinic phase; the second one is a ferromagnetic contribution coming (or originating) from a minority phase, the type I orthorhombic modification of the monoclinic phase (in this case, with the same stoichiometry of the majority phase). In the low-temperature region ($T<268$ K) the magnetization has a strong ferromagnetic character that can be attributed to the type I orthorhombic phase, which is the unique or at least the far majority phase in this temperature region.

Figure 3 shows a sequence of representative ESR spectra. The temperature-dependent results can be also separated in three regions: (*i*) at high temperatures ($T>315$ K) the spectra present clearly only one resonance with a well-characterized Dysonian line shape; (*ii*) in the region of intermediate temperatures (268 K$<T<$315 K) there are at least two rather distinct lines; and (*iii*) at low temperatures (T

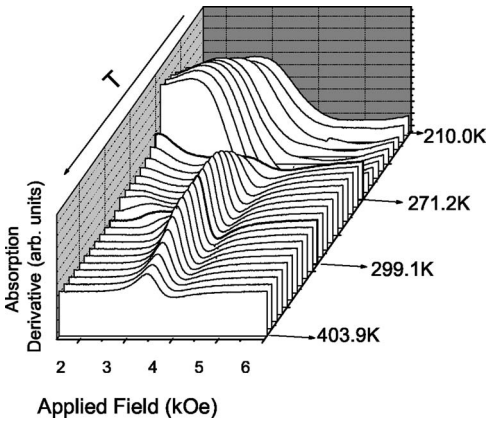

FIG. 3. ESR spectra at different temperatures for the heat-treated sample.

<268 K) there is one very intense symmetrical resonance with small perturbations in the spectra (in some spectra these perturbations have features of a resonance line but their intensities are almost negligible compared to the main broad line). Figure 4 shows typical spectra for these temperature regions.

Figure 5 presents the applied field for resonance (H_{res}) as a function of temperature for the two samples. There is a resonance line which is present both in the paramagnetic and in the intermediary temperature regions. Its H_{res} and the other spectral parameters are equal, within the experimental error, in both regions for both samples. The small dependence with temperature in the H_{res} values of this line between ~268 K and 400 K is a paramagneticlike behavior. Its Dysonian line shape is typical for metals in the PM regime. The values of H_{res} for this paramagnetic line presented in

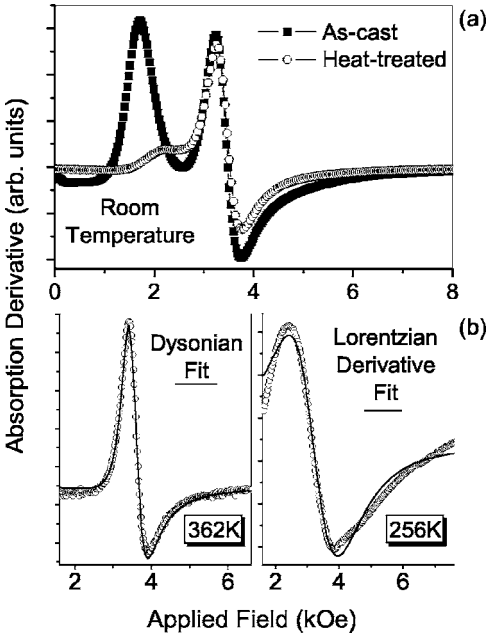

FIG. 4. (a) ESR spectra obtained at room temperature for both samples showing the two lines. (b) Spectra at 362 K and 256 K for the heat-treated sample with the corresponding fits.

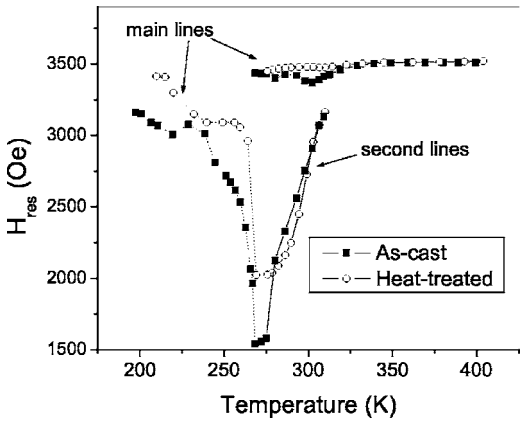

FIG. 5. Applied field for resonance (H_{res}) as a function of temperature for both samples.

Fig. 5 were obtained from Dysonian fits, as the one presented in Fig. 4(b). The correlation coefficients of these fits are close to 1, showing a good description of the experimental data. The measured A/B ratios of low-field to high-field peak heights are close to the theoretical value[9] (2.55) for samples much larger than the skin depth. The interpretation of this resonance line is that it is coming from the two paramagnetic phases present in the sample above 315 K, the main monoclinic phase with stoichiometry 5:2:2 and the type I orthorhombic modification of the 5:2:2 phase, whereas between ~268 K and 315 K it is coming only from the main monoclinic phase.

The marked changes in the H_{res} values of the second line in the intermediary region and the main line in the low temperature region are expected for systems with magnetic order where the magnetization has not reached a stable regime. A tendency to stability of H_{res} for these two lines can be noted below 300 K and 270 K, respectively. These are the same temperatures below which the magnetization curve (Fig. 2) presents a flattening behavior. Although reflecting ordering effects, the changes in H_{res} occur in opposite directions, decreasing in value for one line and increasing for the other one. Then, one can say that each of these lines is related to rather distinct local fields, produced by the different environments of the Gd ions. From 300 K down to 270 K the second line must be attributed to the type I orthorhombic phase (which was already present at high temperature); below 270 K the main line is attributed to the majority type I orthorhombic coming from the monoclinic phase.

In this last region the general behavior of H_{res} is similar for both samples, increasing from 270 K to 200 K, sharply at the beginning and at smaller rates at lower temperatures, displaying an intermediate shoulder. The H_{res} values for the heat-treated sample are always higher than for the as-cast sample. It is also observed that the shoulder of the heat-treated sample occurs at a higher temperature. These differences can be explained by the distinct magnetizations in this temperature region and by the differences in shape (demagnetizing factors) of the samples.

With respect to the second line in the intermediary region, its overlap with the PM line and its fast displacement to low fields as the temperature is decreased prevent an accurate discrimination of its parameters and line shape in the lower temperature interval. However, as there is a greater amount of the type I orthorhombic modification of the 5:2:2 phase in the as-cast sample, the correlation between the second resonance line and this crystallographic phase is clear if one compares its intensity for the two samples [Fig. 4(a)] with the enhancement of the magnetization curve in the intermediary region (Fig. 2). The second-order transition temperature is 302 K, but the presence of this second resonance line shows clear ordering effects already at 315 K.

The main line appearing at low temperatures ($T < 268$ K) has a more symmetric shape, as a derivative of a Lorentzian line, common in the FM regime. This is the case for our samples in the low-temperature region, as shown by the magnetization behavior (Fig. 2). The small perturbation in these spectra can be due to the presence of the second line of the intermediary region.

A tendency to a stability of the effective g value (g_{eff}) at high temperatures (>360 K) was observed and it is another expected paramagneticlike behavior. It is remarkable that even though this tendency occurs, the limiting values at high temperatures (1.888 ± 0.002 and 1.884 ± 0.002, for the as-cast and the heat-treated sample, respectively) are smaller than the g value for noninteracting Gd^{3+} ions in insulating samples ($g_o = 1.992$).[10] A manifestation of the increasing magnetic interaction among the Gd^{3+} ions was also observed in the g_{eff} temperature behavior: there is an abrupt up-turn as the second-order transition approximates. This is a common result around disorder-order transitions.[11,12] It is not possible to make a detailed discussion about the g value in the other two temperature regions, which include ordered phases, also because the shape of the sample is not well defined, preventing an accurate knowledge of the demagnetizing factor.[11]

If one considers that there is no orbital contribution to the total angular momentum of Gd^{3+} ions, i.e., $J = S = \frac{7}{2}$, the measured g_{eff} values at temperatures greater than 380 K correspond to effective magnetic moments of 7.50 and 7.48 μ_B for the as-cast and the heat-treated samples, respectively. The greatest value calculated by Samolyuk *et al.*[13] for $Gd_5Si_2Ge_2$, using the TB-LMTO method with core treatment of 4*f* states, was 7.46 μ_B and the average of the five different Gd^{3+} sites was 7.348 μ_B. Szade *et al.*[7] presented experimental results of 7.89 μ_B from $M(T)$ Curie-Weiss fits for this temperature region. This last magnetic moment is higher than ours, however, the behavior of the magnetization and value of T_C are a little different from those for our samples. Although the Curie-Weiss dependence of temperature provides a good representation of experimental results, it is not clear if this model is quantitatively applicable as pointed out in Ref. 7. Concerning this point, an alternative mean field model including lattice deformation has been proposed to explain the phase transitions in magnetocaloric compounds.[14]

The resonance linewidths (ΔH) for the PM temperature region are presented in Fig. 6. The ΔH behavior as a function of temperature is the same for both samples, although the heat-treated one shows values a little higher. This distinction can be attributed to changes in the crystallites induced by the annealing, since the resonance lines are inhomogeneously broadened due to the distribution of the crystallites demag-

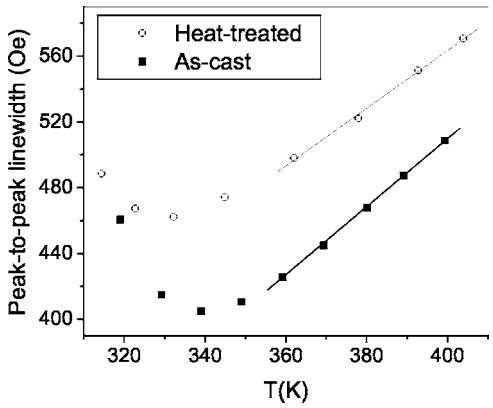

FIG. 6. Measured ESR linewidth in the paramagnetic temperature region.

netizing factors. There is a characteristic minimum below which ΔH increases as a consequence of the arising short range order as the phase transition approximates. Above the minimum the linewidth increases linearly. The observed linear dependence at high temperatures ($T > 360$ K) is expected for metals in the PM regime, but it is not a simple Korringa dependence. In the case of metals with dilute magnetic ions, where the Korringa behavior occurs, the linear part of ΔH curve has the angular coefficient $\pi k_B \Delta g^2 / g_0 \mu_B$, where Δg is the temperature-independent g shift.[11,15,16] The calculated value of that coefficient for our samples did not fit with our experimental value (from Fig. 6). This is probably due to the bottleneck effect which is common in metals with high concentrations of magnetic ions, which also can justify the low effective g values.

Additional comments about the slopes of ΔH at high temperatures can be made. The measured slopes are 2.09 ± 0.02 Oe/K and 1.76 ± 0.06 Oe/K for the as-cast and heat-treated samples, respectively. They are close to each other, as expected, but the difference of about 15% with respect to the value for the as-cast sample cannot be disregarded. Usually an increase of the concentration of the magnetic ions leads to a reduction of the slope.[15,16] For these samples this seems to be the case as the as-cast sample presents a greater amount of the type I orthorhombic modification of the 5:2:2 phase than the heat-treated one.[5]

Additional crystallographic phases, the 2:1:1 in particular, have been identified in samples prepared with the nominal 5:2:2 composition.[4,5] Also, samples of this stoichiometry show the co-existence of the orthorhombic modification of the 5:2:2 phase, whose T_C is ~ 300 K, with the majority monoclinic modification. Heat treatments at high temperatures reduce the amount of the two phases coexisting with the monoclinic one and leads to samples with higher magnetocaloric effect. The fact that the heat-treatment reduces the observed enhancement of the magnetization between the second- and first-order magnetic transitions, and the direct relation observed here between this enhancement and the second resonance line in this region, suggests a correspondence between this line and the orthorhombic modification of the 5:2:2 phase. That means the orthorhombic modification of the 5:2:2 phase is responsible for the manifestation of the second-order magnetic transition.

Levin *et al.*[2,3] have pointed out a range of coexistence of the PM and the FM phases for the 5:2:2 composition. However, this coexistence appears for higher magnetic field values compared with the ones employed in these ESR experiments. So, the two detected resonance lines in the intermediary region of temperature are related to two different crystallographic phases and not to two different magnetic phases of the majority crystallographic phase. The temperature interval of coexistence pointed out by the ESR results is consistent with the interval between the two observed magnetic transitions.

CONCLUSIONS

A characterization of the phase transitions of $Gd_{5.09}Ge_{2.03}Si_{1.88}$ samples has been made correlating magnetization and ESR results. The ESR results permitted a clear distinction of two coexisting phases in the temperature range between the two observed magnetic phase transitions.

The marked variations of the H_{res} and the linewidth of the second resonance line observed in the intermediary temperature region, and the inversion of the predominance between this line and the paramagnetic one in the spectra, were associated to the behavior of a heterogeneous magnetic system composed by a magnetically disordered phase and another ordered one. The second signal was associated to a coexisting minority crystallographic phase, corresponding to the orthorhombic modification of the main monoclinic phase.

Additionally, the measured values for the effective g factor allowed an estimate of the effective magnetic moment at high temperatures in good agreement with the published data.

ACKNOWLEDGMENTS

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