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Spontaneous generation of voltage in $Gd_5(Si_xGe_{4-x})$ during a first-order phase transition induced by temperature or magnetic field

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The spontaneous generation of voltage has been observed during the first-order magnetic-Martensitic phase transition process in $Gd_5(Si_xGe_{4-x})$ alloys regardless of whether the transformation is triggered by temperature or magnetic field. Based on various experimental data we show that thermoelectric power is a major contributor to the observed voltage. The characteristics of the simultaneously recorded spontaneous voltage and the signal from a differential thermocouple attached to the sample are quite complex, indicating that thermal effects arising in this class of materials during the first-order phase transition are nontrivial. The unusual dynamics of both the heat release and absorption during the phase transformations in $Gd_5(Si_xGe_{4-x})$ result in the appearance of temperature gradients and, therefore, thermoelectricity.

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I. INTRODUCTION

Complex intermetallic compounds of the $4f$ and $5f$ elements often exhibit intriguing electrical behavior, which can be particularly striking during first-order phase transitions.[1–3] Among these are $Gd_5(Si_xGe_{4-x})$ intermetallics discovered in 1967 (Ref. 4) and recently recognized as exceptionally complex systems where unusual physical properties are intimately related with the chemical composition and uniquely layered crystal structures of the materials.[5–14] The temperature of the first order phase transition in $Gd_5(Si_xGe_{4-x})$, when $0 \leqslant x \leqslant 2$, strongly depends on x.[5,11,14] Ferromagnetic (FM) and paramagnetic (PM) phases coexist during the transition when $0.96 \leqslant x \leqslant 2$, as do the FM and antiferromagnetic (AFM) phases when $0 \leqslant x \leqslant 0.8$.[8,11,13] The crystallographic transition occurs via the breaking/reforming of specific Si(Ge)-Si(Ge) bonds and results in a large (~0.8 to 1.1 Å) movement of the subnanometer thick atomic slabs.[12,13] Both the magnetic and crystal structure at $x=$const are easily effected by temperature and/or magnetic field[6,11–13] indicating strong coupling between the magnetic and crystal lattices, and dynamic changes of both the magnetic and crystallographic parameters of such system can bring to light novel physical phenomena.

In this paper we report on an unusual electrical effect—a spontaneous electromotive force, which is observed in the $Gd_5(Si_xGe_{4-x})$ alloys during a first-order phase transition *regardless of whether this transition is triggered by temperature or by a magnetic field*. Although the phase transition is induced by an external force (magnetic field or temperature), the measured voltage is intrinsic to the phase transition process and, therefore, is generated spontaneously during the nonequilibrium phase change progressing through the specimen.

II. EXPERIMENTAL DETAILS

Samples of polycrystalline $Gd_5(Si_xGe_{4-x})$ alloys with $x=2$, 1.95, 1.5, 0.33, and 0 were prepared by arc melting[10,11] and then heat treated at 1270–1570 K for 1 to 3 h. Two to four electrical connections using various samples with different shapes (parallelepiped, cube, plate) and dimensions ($1\times1\times4$ to $2\times2\times6$ mm^3) were made using silver epoxy as described in Refs. 8, 10. The voltage measurements with *no* dc *or* ac *current supplied to the sample* were taken between various combinations of leads including simultaneous recording of two signals between different pairs of contacts. Resistance of the samples ranged from 0.03 to 1 Ω, and contact resistance was between 3 and 5 Ω. The temperature of the samples and the magnetic field were controlled using a Lake Shore Model 7225 magnetometer. The rate of temperature change (heating and cooling) was varied from 1 to 3 K/min. The rate of isothermal magnetic field change was approximately 40 kOe/min. The temperature gradient along the sample between the voltage measuring leads was measured using differential chromel-alumel thermocouples. The thermocouple wire diameter was ~60 μm and the two junctions were attached in the proximity of the voltage measuring leads enabling simultaneous recording of the two signals, i.e., the voltage across the sample and the thermal electromotive force (EMF) of the differential thermocouple. At equilibrium, i.e., both before and after the phase transition, the temperature gradient along the sample did not exceed 0.1 K, while temperature gradients from 0.3 to 0.5 K were observed during the transition.

The dc voltages were measured parallel or perpendicular to the magnetic field vector as a function of time using a digital Keithley 181 voltmeter with 0–1 V analog output coupled to a Fisher Y-time recorder. Signal changes of 0.05 μV and greater were clearly distinguished. The dc voltage was recorded both with the background due to small temperature gradient and with the background subtracted after the voltmeter was zeroed for compensation. The typical amplitude of the background voltage in the isothermal regime was ~0.5 μV rising up to ~1 μV in the isofield regime. The voltage arising from the Faraday effect due to the changing of the magnetic flux through the electrical contacts and the

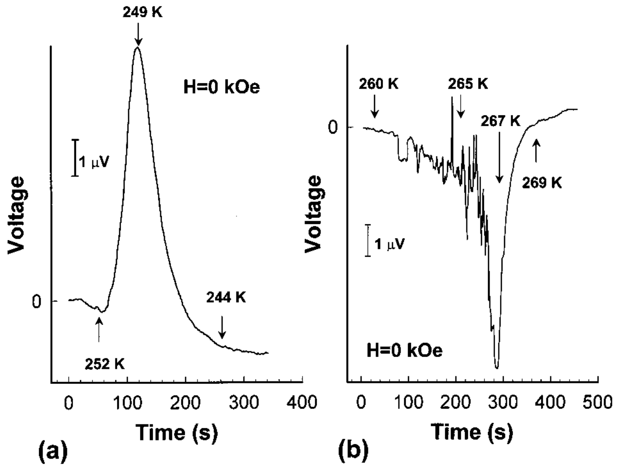

FIG. 1. The spontaneously generated voltage (SGV) during the first-order magnetic-Martensitic phase transition in $Gd_5(Si_{1.95}Ge_{2.05})$ triggered by a temperature change in zero magnetic field on cooling (a) and heating (b). The magnitude of 1 μV is indicated in both plots.

sample is easily detected at the beginning and at the end of the magnetic field sweeps and does not exceed 0.5 μV.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The four samples of $Gd_5(Si_xGe_{4-x})$ alloys with $x=2$, 1.95, 1.5, and 0.33 used in this study undergo simultaneous magnetic-Martensitic transformations in zero magnetic field on heating at ~276, 266, 217, and 69 K, respectively.[14] The fifth sample, with $x=0$, has somewhat different behavior, and the first order magnetic-Martensitic transformation in this material occurs only in magnetic fields of 20 kOe and higher. The spontaneously generated voltage (SGV) has been observed in all five samples during either or both the temperature and magnetic field induced first order phase transformations. Although, the observed signals depend on the composition of the alloy, the major difference is in the temperature where the SGV is observed. Therefore, practically all experimental results shown below were collected using the $Gd_5(Si_{1.95}Ge_{2.05})$ composition.

The temperature dependencies of the spontaneously generated voltage (SGV) in $Gd_5(Si_{1.95}Ge_{2.05})$ during cooling and heating through the first order phase transition at a constant rate of ~1.5 K/min in zero magnetic field are shown in Fig. 1. A nearly symmetrical peak reaching 8 μV at ~249 K is observed on cooling [Fig. 1(a)]. On heating, the signal has the opposite polarity and its behavior is much more complex [Fig. 1(b)]. First, several random spikes between 262 and 266 K and then a large main peak reaching -6 μV at ~267 K are clearly visible. When the measurements are carried out in a constant 20 kOe magnetic field, the signals are shifted by ~12 K towards higher temperatures, which is expected because the magnetic field raises the phase transition temperature of $Gd_5(Si_xGe_{4-x})$ materials by ~0.5–0.6 K/kOe.[5–8,10] The SGV behavior on both heating and cooling shown in Fig. 1 is well reproducible during repeated measurements except for the magnitude and the location of random spikes observed on heating. We also note an ~18 K temperature hysteresis between heating and cooling. Similar voltages were observed in $Gd_5(Si_2Ge_2)$ and $Gd_5(Si_{1.5}Ge_{2.5})$ at their first-order phase transition temperatures. When heating is carried out at a faster rate, ~3 K/min, the amplitude of the SGV peak in all samples is increased.

To the best of our knowledge, only few observations of the spontaneous voltage were ever reported. Its history could be traced to single crystalline FeS,[15] where voltage generation occurs during temperature induced crystallographic phase transition between 413 and 428 K. Voltage pulses during temperature induced transitions were also observed in shape memory TiNi (Ref. 16) and FeNi (Ref. 17) alloys during Martensitic transitions, and in Ce during the $\gamma \leftrightarrow \alpha$ valence phase transition.[18] Hence, in all cases, the SGV is the result of dynamical changes in the material occurring during first order phase transitions induced by temperature. The nature of materials where it was observed is quite different, and so are the explanations, suggested by the various authors. For example, in FeS the thermoelectric power was excluded and a diffusion model was proposed.[15] The voltage generation in FeNi was associated with the thermoelectric power,[17] while the experiment with TiNi (Ref. 16) virtually eliminates thermoelectric power effects. Furthermore, in Ref. 16 it was suggested that the voltage arises from the motion of twin boundaries in TiNi. A dc voltage was also observed during the temperature-induced first-order phase transitions in Sn, CuBr, $YBa_2Cu_3O_7$, and water,[19] and the authors associate this voltage with Seebeck effect, i.e., thermoelectric power. The list of materials reported to display this unusual electrical phenomenon is short, but does include both metallic (TiNi, FeNi, Ce, and Sn) and nonmetallic (FeS, CuBr, $YBa_2Cu_3O_7$, and H_2O) substances. We note also that the phase transitions in these materials do not include a magnetic phase change.

As was shown in Refs. 5–8,10,13, a magnetic field applied just above the Curie temperature effects both the magnetic and crystallographic phases in $Gd_5(Si_xGe_{4-x})$. Therefore, the voltage in this class of materials should be also generated isothermally by a magnetic field. The SGV of the $Gd_5(Si_{1.95}Ge_{2.05})$ sample at $T=270$ K in a varying magnetic field is shown in Fig. 2. Increasing the magnetic field simultaneously triggers the magnetic PM→FM and crystallographic monoclinic→orthorhombic phase transitions, and the voltage [Fig. 2(a)] is similar to that observed on cooling [Fig. 1(a)]. When the magnetic field is removed, the signal changes polarity [Fig. 2(b)]. Several random voltage spikes, and a main peak are detected. The behavior during field reduction closely resembles that observed during heating [Fig. 1(b)], which is expected because the high magnetic field (i.e., low temperature) FM orthorhombic phase transforms into the low magnetic field (i.e., high temperature) PM monoclinic phase. The random spikes are broader due to the higher transformation rate (compare time scales in Figs. 1 and 2). The SGV behavior is insensitive to a 180° change of the magnetic field vector direction and is dependent only on the sign of the magnetic field change (i.e., its increase or reduction).

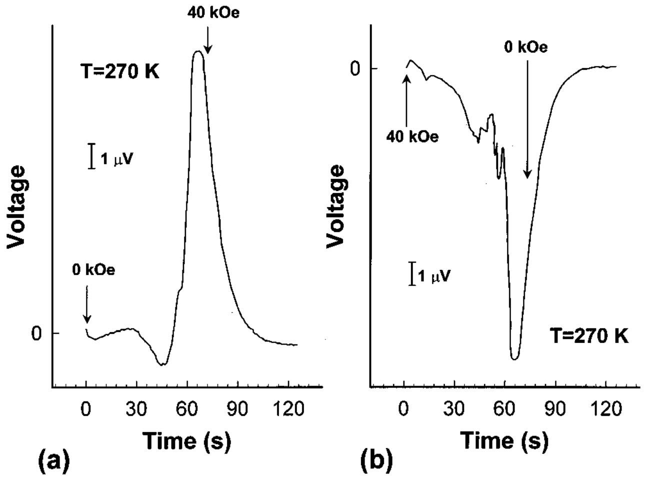

FIG. 2. The spontaneously generated voltage during the first order magnetic-Martensitic phase transition in $Gd_5(Si_{1.95}Ge_{2.05})$ triggered by a magnetic field change at 270 K on a field increase (a) and reduction (b). The magnitude of 1 μV is indicated in both plots.

The position of the main SGV peak is a function of both magnetic field and temperature, which is shown in Fig. 3. The critical magnetic fields, taken as the SGV peaks, increase with temperature. Thus determined critical magnetic fields are in fair agreement with the phase diagram of $Gd_5(Si_{1.95}Ge_{2.05})$ based on the magnetization data[20] and are shown in Fig. 4. The positions of the main voltage peaks observed during isothermal increase and reduction of the magnetic field are shown as solid and opened squares, respectively. The lines marked PF_s and FP_s indicate the start, and PF_f and FP_f the finish of PM↔FM phase transformation process when the magnetic field increases or decreases, respectively, as established from isothermal magnetic measurements carried out at equilibrium. The areas between PF_s and PF_f, and FP_s and FP_f delineate the magnetically heterogeneous regions where FM and PM phases coexist. We note that the phase diagram (Fig. 4) is typical for other $Gd_5(Si_xGe_{4-x})$ alloys.[8,10] It is easy to see that the maximum SGV is observed close to the lines indicating the end of the respective phase transformation, and the position of the maximum observed during nonequilibrium phase change likely reflects the highest rate of the transformation process.

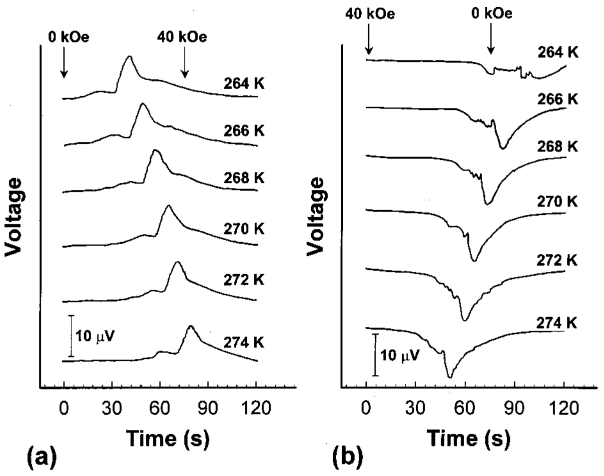

FIG. 3. The spontaneously generated voltage during first-order magnetic-Martensitic phase transition in $Gd_5(Si_{1.95}Ge_{2.05})$ triggered by a magnetic filed change at different temperatures on a field increase (a) or reduction (b). The magnitude of 10 μV is indicated on both plots.

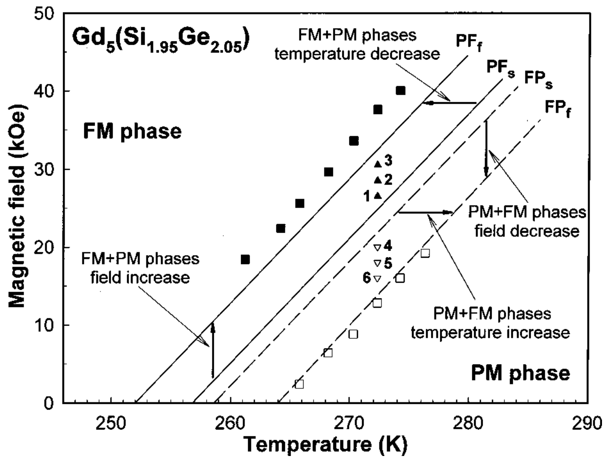

FIG. 4. The magnetic phase diagram of $Gd_5(Si_{1.95}Ge_{2.05})$. The solid lines indicate the start and the end of PM→FM transformation (PF_s and PF_f) and the dashed lines represent the start and the end of FM→PM transformation (FP_s and FP_f), respectively. The positions of SGV peaks observed during isothermal increase (filled squares) or reduction (open squares) of the magnetic field between 0 and 40 kOe are shown. The filled and opened triangles indicate the values of the specific magnetic fields H_i and H_d where $Gd_5(Si_{1.95}Ge_{2.05})$ is heterogeneous (i.e., consist of the FM orthorhombic and PM monoclinic phases) at 272.3 ± 0.2 K (also see Fig. 5).

The character of the SGV behavior during a magnetic field increase at ~264 K, i.e., the presence of a well defined peak, indicates that the magnetic field change completes the PM→FM transformation of $Gd_5(Si_{1.95}Ge_{2.05})$. The magnetic field reduction at the same temperature, however, indicates a much slower reverse transformation as is evident from the presence of extended random spikes of the SGV. This conclusion correlates well with the equilibrium phase diagram (see Fig. 4) which shows that reduction of the magnetic field to zero at ~264 K retains the system just between the two-phase (FM+PM) and paramagnetic regions. Figure 3 also shows that the phase transformation process continues even when the magnetic field was stopped at 40 kOe [see the isotherms at 272 and 274 K, Fig. 3(a)] or at zero [see the isotherms at 268 K and below, Fig. 3(b)]. The results presented in Fig. 3 combined with the phase diagram shown in Fig. 4, therefore, indicate that the magnetic-Martensitic first-order phase transformation in $Gd_5(Si_{1.95}Ge_{2.05})$ has finite kinetics.

The ability of the magnetic field to effect the phase equilibrium isothermally provides an excellent tool for probing the behavior in the magnetically heterogeneous regions using the SGV response. The magnetic field can be rapidly adjusted and then fixed to ''freeze'' the system containing the two phases in various ratios. The results obtained at *T*

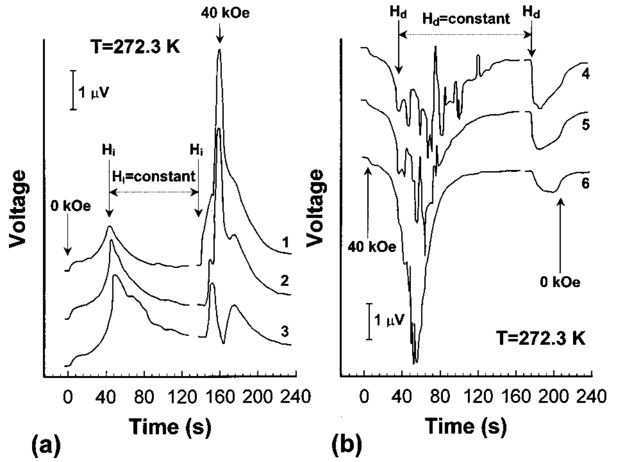

FIG. 5. The SGV signals observed during a rapid magnetic field increase from 0 to H_i (where $H_i = 26$ kOe for curve 1, 28 kOe for curve 2, and 30 kOe for curve 3), holding at H_i long enough for PM+FM phase equilibrium to be established, followed by a rapid magnetic field increase from H_i to 40 kOe (a). The same is shown in (b) for a magnetic field decrease from 40 kOe to H_d (where $H_d = 20$ kOe for curve 4, 18 kOe for curve 5, and 16 kOe for curve 6), then holding at H_d long enough for FM+PM phase equilibrium to be established, followed by a rapid magnetic field decrease from H_d to zero. The numbering of SGV curves corresponds to the numbering of filled and opened triangles in Fig. 4. The magnitude of 1 μV is indicated in both plots.

$= 272.3 \pm 0.2$ K (the field values are shown as closed and opened triangles in Fig. 4) are shown in Fig. 5. The two-phase region where PM→FM transformation takes place was probed by recording the SGV as follows. First, the magnetic field was rapidly increased from zero to a specified H_i [see Figs. 4, 5(a)]. Second, the system was allowed to stabilize in the two-phase region at $H_i = \text{const}$. Finally, the magnetic field was rapidly ramped from H_i to 40 kOe to complete the transformation. The two-phase region where FM→PM transition occurs [Figs. 4 and 5(b)] was studied in a similar fashion during magnetic field reduction from 40 kOe to zero holding the sample in different constant magnetic fields $0 < H_d < 40$ kOe.

In the two-phase region during PM→FM transformation, the magnitude of the first SGV peak increases continuously in line with the rising transformation rate and the amount of the formed FM phase [Fig. 5(a)]. The magnitude of the second peak (indicating the transformation of the remainder of the PM phase into the FM phase) is accordingly reduced. In the two-phase region during FM→PM transformation, the random SGV spikes continue for 1–2 min after the magnetic field was set at $H_d = 20$ and 18 kOe [Fig. 5(b)]. The number and the duration of random voltage spikes decreases as the amount of FM phase transformed in the PM phase increases and a main peak becomes well defined for $H_d = 16$ kOe [Fig. 5(b)]. When the magnetic field is further reduced from H_d to zero, the sample generates voltage again but the amplitude of the second peak decreases in line with the reduced amount of the remaining nontransformed FM phase. Therefore, the observed SGV behavior (i) provides a direct proof that PM and FM phases indeed coexist in a certain temperature and magnetic field intervals, and also (ii) shows considerable differences between the kinetics and the mechanism of the PM→FM and FM→PM phase transformations. Furthermore, since the voltage disappears as phase equilibrium established even in the two-phase region (Fig. 5), its presence and behavior reflects the changes occurring in the system when the amount of one phase increases while the amount of the second phase decreases.

As obvious from Figs. 2, 3, and 5, the voltage generation may continue even when magnetic field is stopped, which enables one to conclude that this electrical phenomenon is the result of a nonequilibrium phase transformation process developing spontaneously in the corresponding direction (PM→FM or FM→PM). The observed times required for the SGV to relax from its maximum to zero at constant temperature and magnetic field are on the order of 30 s to 3 min. Taking into account that $Gd_5(Si_{1.95}Ge_{2.05})$ is metallic, the relaxation time is extremely long which further suggests that the voltage is indeed spontaneous and is not purely electronic in nature because electronic relaxation times in metals are usually on the order of 10^{-12} s.

The SGV was also observed in other studied polycrystalline $Gd_5(Si_xGe_{4-x})$ samples at temperatures ranging from 30 to 280 K where the magnetic field induces the reversible PM↔FM ($x = 2, 1.5$) or AFM↔FM ($x = 0.33, 0$) first-order phase transitions. Figure 6 illustrates the voltage recorded in four different $Gd_5(Si_xGe_{4-x})$ samples at temperatures where the alloys are either antiferromagnetic ($x = 0$ and 0.33) or paramagnetic ($x = 1.5$ and 2) in zero magnetic field and are completely transformed into the ferromagnetic state by the application of 40 kOe magnetic field. Despite the fact that the SGV is somewhat different from one sample to another (i.e., its behavior as a function of magnetic field varies from a sharp peak to a broad peak(s) and even *S*-shape functions, see Fig. 6), it is well reproducible for the same sample during repeated cycling through the first-order phase transition. Preliminary data obtained using a single crystal of $Gd_5(Si_{1.95}Ge_{2.05})$ indicate that SGV is anisotropic and the effect is stronger when measured along the *b* axis, i.e., perpendicular to the slabs. The maximum observed absolute SGV value was ~16 μV. In all cases, the SGV has the same polarity for both heating in a constant field and for an isothermal magnetic field reduction. The polarity is reversed during cooling in a constant field and for an isothermal magnetic field increase. All available experimental data suggest, therefore, that the SGV has the same nature in all $Gd_5(Si_xGe_{4-x})$ samples and depends on the direction in which the system crosses the phase boundaries (i.e., heating/demagnetizing or cooling/magnetizing). As shown by Morellon *et al.*,[6] the hydrostatic pressure also induces the magnetic-crystallographic transformation in $Gd_5(Si_{1.8}Ge_{2.2})$ and, therefore, we predict that the SGV will be observed in the $Gd_5(Si_xGe_{4-x})$ materials in response to pressure changes. No SGV was detected for second-order transitions, e.g., near 130 K for both $Gd_5(Si_{0.33}Ge_{3.67})$ and Gd_5Ge_4.

Although more detailed experimental and theoretical studies are required before the nature of the SGV is fully understood, the similarity of the processes occurring during the first-order phase transition in the studied $Gd_5(Si_xGe_{4-x})$ ma-

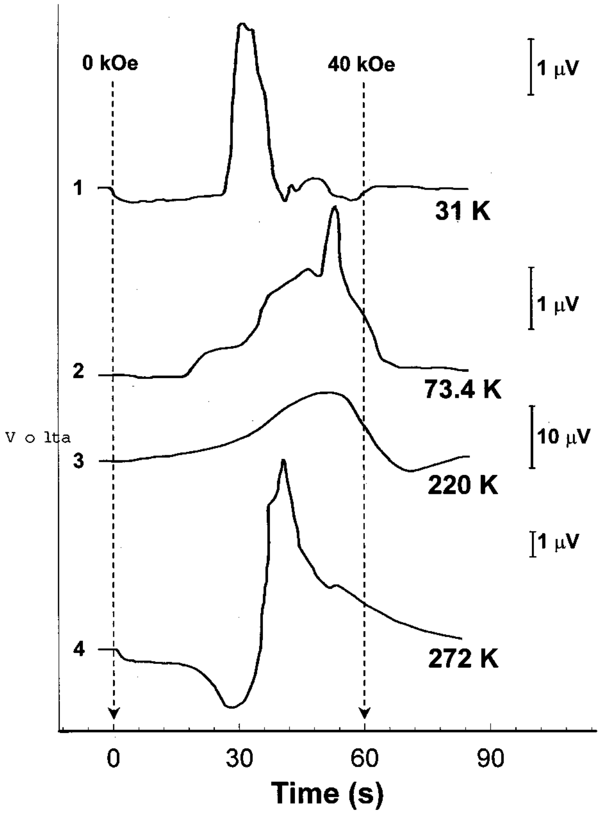

FIG. 6. The spontaneously generated voltage during the first-order magnetic-Martensitic phase transition in Gd_5Ge_4 (curve 1), $Gd_5(Si_{0.33}Ge_{3.67})$ (curve 2), $Gd_5(Si_{1.5}Ge_{2.5})$ (curve 3), and $Gd_5(Si_2Ge_2)$ (curve 4) triggered by a magnetic field increase at different temperatures. The magnitudes of 10 and 1 μV are indicated for the corresponding plots.

terials enables at least a qualitative understanding. First, different phases with high (FM) and low (PM or AFM) magnetization coexist in the same sample and the fraction of each is easily controlled by varying temperature and/or magnetic field. Second, the phases coexisting in $Gd_5(Si_xGe_{4-x})$ have different crystal structures, and the phase change is associated with breaking/reforming of chemical bonds. Third, based on the bonding differences between the coexisting phases, the electronic structure and, therefore, the charge carrier concentration could be considerably different in the two phases. Fourth, discontinuous changes of the respective derivatives of the Gibbs free energy and, therefore, the enthalpy and volume occur in all systems.

Several possible mechanisms of the SGV effect can be envisioned. The first one is the giant thermal fluctuations of voltage, and the second one is the contact potential difference. Both are unlikely to contribute significantly to the effect because in all experiments the voltage is clearly dependent on the rate and the direction of the first-order phase transition. Furthermore, according to our data, the current-voltage dependencies (two-probe measurements) are linear in the two-phase regions at equilibrium, i.e., there are no Schottky barriers. Another possible phenomenon is conduction electron density gradient occurring between different (both crystallographically and magnetically) phases, which is a model similar to that proposed by Takahashi and Yamada for FeS.[15] Conduction electron density gradients are feasible in the $Gd_5(Si_xGe_{4-x})$ alloys because phase transformations in these systems are associated with drastic changes in chemical bonding. The effect of varying the internal magnetic field flux through the sample (the internal Faraday effect) can also contribute to the SGV. None of the mechanisms considered above, however, supports the possibility of breaking the symmetry of the SGV in polycrystalline materials, unless one assumes that the samples are slightly inhomogeneous, textured, or there is an intrinsic and constant temperature gradient across the sample during measurements. This brings about another possible explanation of the mechanism of the observed spontaneous voltage, i.e., the thermoelectric power.

Thermoelectric power, despite an obvious possibility that the varying temperature gradient may arise during the phase transition due to enthalpy difference between the two phases if the transition originates in a specific part of the sample and then propagates in a specific direction through the entire specimen, was not our first choice for an explanation of the SGV. This was particularly difficult to assume because the measured equilibrium temperature gradient was rather small (i.e., about 0.1 K, see above) and because of distinct and rapid SGV spikes observed during FM→PM transitions [Figs. 1(b), 2(b), 5(b)]. The spikes could be caused only by extremely unusual transformation mechanism assuming a rapid, almost explosive nucleation and growth of the PM phase in the FM matrix lowering local temperature in a specific part of the sample followed by equally explosive disappearance of the PM nuclei causing rapid reversal of both the local temperature and the overall temperature gradient. It is clear that the amplitude of the enthalpy change and possible local and long-range temperature gradients should be dependent on texture and local chemical homogeneity of the sample, while their signs depend on the direction of the phase transition. Hence, we performed a series of measurements of the temperature gradients between the electrical connections simultaneously with the SGV.

Figure 7 shows the result of these measurements for the $Gd_5(Si_{1.95}Ge_{2.05})$ sample where the generated voltage and the signal from a differential thermocouple are plotted together during magnetic filed reduction in the isothermal regime from 40 kOe to 0 [Fig. 7(a)] and from 40 to 20 kOe [Fig. 7(b)] at ~270 and ~272 K, respectively. The observed shape of the SGV peak [Fig. 7(a)], in general, is similar to that observed for the sample without the attached thermocouple [see Fig. 2(b)]. It is obvious that the peak of the SGV occurs simultaneously with the peak of the thermocouple voltage. Hence, it is safe to conclude that the temperature gradient consistent with the behavior of the SGV appears between the electrical connections to the specimen. Similar peaks in both SGV and thermocouple are also observed at 268 and 272 K during both magnetic field increase and reduction and, therefore, we can conclude that Seebeck effect (i.e., thermoelectrical response of the measured sample) plays a major role in the appearance of the spontaneously generated voltage. To verify whether the SGV spikes are due to the explosively

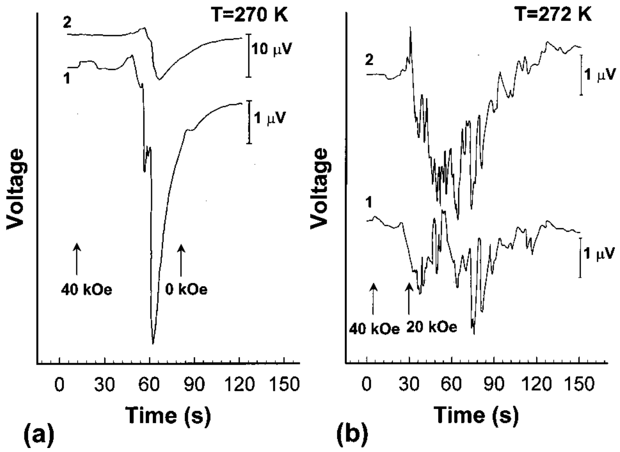

FIG. 7. The spontaneously generated voltage during the first-order magnetic-Martensitic phase transition in $Gd_5(Si_{1.95}Ge_{2.05})$ triggered by a magnetic field change (curves 1) and the voltage from a differential thermocouple measuring temperature gradient between electrical connection (curves 2) recorded simultaneously during magnetic field decrease from 40 to 0 kOe at 270 K (a) and from 40 to 20 kOe at 272 K (b). The magnitudes of 10 and 1 μV are indicated for the corresponding plots.

varying temperature gradient, we repeated the experiment with incomplete phase transformation, which is shown in Fig. 5(b), but this time simultaneously with the SGV, the signal from the differential thermocouple was also recorded. In Fig. 7(b) we show the behavior of both signals when the magnetic field at ~272 K was reduced from 40 to 20 kOe (see also Fig. 5, curve 4). When the magnetic field was stopped in the two-phase region, both the SGV and the signal from the thermocouple indicate a sporadic behavior. It is quite surprising that the differential thermocouple enables detection of even the random spike structure similar to that observed for the spontaneously generated voltage. Although in this case both signals, i.e., SGV and from the differential thermocouple, do not fully coincide, the result supports the conclusion that the main reason for the observed SGV phenomena in the $Gd_5(Si_xGe_{4-x})$ materials is *the unusual dynamics of the heat release and absorption during the phase transformation, which results in the appearance of the temperature gradients and, therefore, thermoelectricity*. We note that the thermal phenomena (i.e., local and long-range heat release and absorption, the rate of the phase transformations, distribution of heat flows, relationship between local thermal and electrical fields, etc.) are quite complex in these alloys, and more detailed studies are required for their understanding.

The differential thermocouple attached to the sample also shows that even in the isothermal regime and away from the phase transition (i.e., at equilibrium) a small temperature gradient (less than 0.1 K) is present across the sample. This constant gradient is most likely due to the presence of the temperature gradient across the sample holder rod, which is at ~4.2 K near the middle of its length, approximately 50 cm above the sample. The later is unavoidable considering the design of the magnetometer. The presence of small but intrinsic equilibrium temperature gradient along the sample enables an understanding of the breaking of the symmetry of the SGV, since it determines the ''colder'' and the ''hotter'' sides of the sample.

Consider the two transformations triggered by an isothermal change of the magnetic field. The sample is in the paramagnetic state above its Curie temperature and the magnetic field is increased beyond the critical field triggering PM→FM transition. Since the value of the critical magnetic field increases with temperature (see Fig. 3), then the PM→FM transformation will begin at the ''colder'' side of the sample. After the equilibrium is restored, the ''hotter'' and the ''colder'' sides of now ferromagnetic specimen are the same as those of the paramagnetic specimen. The magnetic field is then reduced triggering the reverse FM→PM transition and this transformation will begin at the ''hotter'' side of the sample. Hence, the phase transition begins in different locations in the specimen depending on the direction of the phase transition, thus reversing the polarity of the generated voltage. Also, different shapes of the SGV signals observed during our experiments with different $Gd_5(Si_xGe_{4-x})$ samples can be caused by both the characteristics of the sample and by the slightly different conditions of the experiments, i.e., by the different equilibrium temperature gradients experienced by different samples. In our experimental setup the sample is mounted on a plastic sample holder and, therefore, some heat exchange will always occur during the measurement between the sample and the holder. Hence the character of this heat exchange can also be one of the important factors determining the shape of the SGV.

The presence of the random spikes before the main peak during the FM→PM and their absence during the PM→FM transitions reflects considerable difference in their mechanisms. Hence, the behavior of the SGV may be, in principal, used for studying of the mechanism and kinetics of the magnetic field or temperature induced transformations in materials with first-order phase transitions similarly to the recently suggested thermoelectric voltage spectroscopy, which was proposed for studying compensation in semi-insulating wide energy band gap semiconductors.[21] We also note that the anomalous voltage generation due to Seebeck effect can be also induced by laser[22] or heat flux through the sample[23] in $YBa_2Cu_3O_x$ materials. It is, therefore, feasible that regardless of its origin the effect of the induced thermoelectric voltage may be useful for power generation, cooling, heat pumping, heat flow measurements, imaging detectors and sensors.[22,23]

IV. CONCLUSIONS

In summary we note that the spontaneously generated voltage observed during the first-order magnetic-martensitic phase transitions in metallic $Gd_5(Si_xGe_{4-x})$ materials is a nonequilibrium electrical effect which exist regardless of whether the transition is triggered by temperature or magnetic field. The shape of the electrical signal, in general, coincides with the temperature gradient along the specimen, indicating that the thermoelectricity is the main reason for the observed phenomenon. However, the complex character of both the SGV and thermocouple signals observed for various $Gd_5(Si_xGe_{4-x})$ samples reflects the nontrivial nature of the thermal effects in this class of materials during the first-order phase transition. The results presented above together with earlier reports also suggest that the effect of the generated voltage may be intrinsic to any nonequilibrium first-order phase transition process. In addition, using $Gd_5(Si_xGe_{4-x})$ materials we show that spontaneously generated voltage can be triggered not only by temperature, but also by the magnetic field.

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