

Anisotropy of the Magnetoresistance in $\text{Gd}_5\text{Si}_2\text{Ge}_2$

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The observed magnetoresistance of single crystalline $\text{Gd}_5\text{Si}_2\text{Ge}_2$ is negative and strongly anisotropic. The absolute values measured along the [100] and [010] directions exceed those parallel to the [001] direction by more than 60%. First principles calculations demonstrate that a structural modification is responsible for the anisotropy of the magnetoresistance, and that the latter is due to a significant reduction of electronic velocity in the [100] direction and the anisotropy of electrical conductivity.

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Giant magnetocaloric [1,2], substantial magnetoresistance (MR) [3,4], and colossal magnetostrictive [5,6] effects, observed in some $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ compounds, prompted further research that resulted in the discovery of many unusual physical behaviors near ferromagnetic (FM) ordering temperature, which is a function of composition within this series of alloys [7–20]. The strong dependence of physical properties on magnetic field opens a potential for applications of $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ and related materials in magnetic refrigeration, magnetoelectrical devices, and magnetomechanical devices, and simultaneously calls for the development of a coherent approach in order to understand their unique magnetoresponsiveness. In addition to magnetic field, large changes of magnetization, electrical resistance, and shape can be triggered in this series of materials by variation of temperature [1–9] and hydrostatic pressure [11,12] around T_C . The exceptional sensitivity of physical properties to a range of intensive thermodynamic variables has been correlated to the first-order martensiticlike structural change, which accompanies FM ordering when $x \leq \sim 2.0$ in the $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ system [5,8,10,14].

Earlier studies of polycrystalline $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ compounds with $x = 0.4$ [15], 1.5 [16], 1.8 [3], 1.95 [17], and 2.0 [4] point to a negative MR with values reaching -50% [15]. However, preferred orientation and grain boundary effects may be dominant in polycrystalline samples, thus masking the intrinsic magnetotransport properties (e.g., see Ref. [16], where the MR of a polycrystalline sample with $x = 1.5$ is positive, the only such example among all compounds from this series studied to date). In this Letter, we report first experimental evidence of the anisotropic MR of the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ compound and show that it can be reproduced from first principles by calculating diffusion conductivity in the low- and high-temperature phases or in the high- and low-magnetic-field phases. The proposed model, considering the contributions from crystal structure and magnetic ordering

changes, facilitates a microscopic explanation of the anisotropic MR in $\text{Gd}_5\text{Si}_2\text{Ge}_2$.

$\text{Gd}_5\text{Si}_2\text{Ge}_2$ single crystal was grown by the Bridgman method from a polycrystalline stock with the same nominal composition. The Curie temperature of the as-grown crystal indicates a nearly ideal $\text{Gd}_5\text{Si}_2\text{Ge}_2$ stoichiometry. The samples were extracted from several large grains of the same batch by using the spark-eroding technique. The three single crystals had a rectangular shape with the longest dimensions parallel to [100], [010], and [001] crystallographic directions, respectively. Electrical resistance was measured on heating and cooling, as well as isothermally, by means of a standard dc four-probe method. The electrical contacts were prepared by using silver epoxy and platinum wires. The magnetic field varied from -40 to 40 kOe, and the temperature from 4.2 to 320 K. A constant dc current of 10 mA was employed in

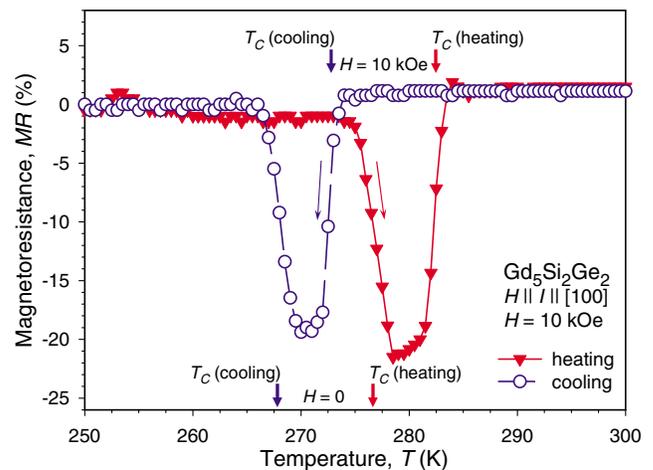


FIG. 1 (color online). The MR ratios of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ measured along the [100] direction on heating and cooling in 0 and 10 kOe magnetic fields. The individual T_C 's and temperature changing directions are marked with arrows.

all the measurements. The current vector was collinear with the magnetic-field direction and the longest dimensions of the specimens in all cases. The magnetoresistance ratio was calculated as $MR(\%) = (\rho_H - \rho_0) / \rho_0 \times 100$, where ρ_H and ρ_0 are the electrical resistivities measured in a magnetic field H and in a zero magnetic field, respectively.

MR ratios along the [100] direction measured on heating and cooling in magnetic fields 0 and 10 kOe are plotted against temperature in Fig. 1. The corresponding zero-field and 10 kOe T_C values determined from the maximum of $d\rho/dT$ are also marked on the plot. A negative MR of -22% at ~ 280 K is observed between the $T_C(0 \text{ kOe})$ and $T_C(10 \text{ kOe})$ on heating and of -20% at ~ 270 K on cooling. A ~ 10 K hysteresis in the MR minima is consistent with the hysteresis in T_C —a characteristic feature of a first-order transformation—which also is observed in other physical properties of polycrystalline $Gd_5Si_2Ge_2$ samples.

Temperature dependencies of MR along the three principal crystallographic directions of $Gd_5Si_2Ge_2$ measured on heating in 0 and 20 kOe fields are compared in Fig. 2. The temperatures in Fig. 2 have been normalized by subtracting the individual zero-field T_C values measured on heating, which were slightly different for three different specimens used in this study, most likely due to a

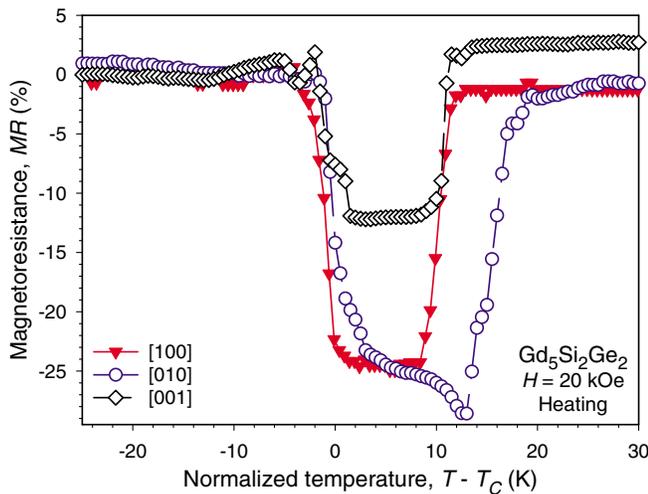


FIG. 2 (color online). The MR ratios of $Gd_5Si_2Ge_2$ as functions of temperature measured along different crystallographic directions on heating in 0 and 20 kOe magnetic fields. The temperatures were normalized by subtracting the individual zero-field T_C values, which are as follows: 278.6 K ([100]), 269 K ([010]), and 276.5 K ([001]), indicating, respectively, the following actual stoichiometries: $Gd_5Si_{2.03}Ge_{1.97}$, $Gd_5Si_{1.97}Ge_{2.03}$, and $Gd_5Si_{2.02}Ge_{1.98}$ [13]. Transport measurements of polycrystalline samples with a much larger variance of the chemical compositions, from $Gd_5Si_{1.8}Ge_{2.2}$ [3] to $Gd_5Si_2Ge_2$ [4], show that, except for a systematic change of the Curie temperature, the Si:Ge ratio has a negligible effect on the electronic transport behavior.

small variation in the Si:Ge ratio. In all the cases, a minimum is observed around the Curie temperature. It is also clear that the temperature dependence of the MR ratio is strongly anisotropic. The maximum absolute values of the MR along the [100] and [010] directions (25% and 28%) are much larger than 13% measured along the [001] direction. The MR signal measured parallel to the [010] direction is also slightly broader than the other two. Although potentially intrinsic to the material (the [010] direction is unique since it is nearly perpendicular to the slabs [7]), this feature could be related to a difference in the stoichiometry, which appears to be the greatest for this particular specimen as judged from its low T_C , and therefore, extrinsic.

The magnetic-field dependencies of the MR ratios measured ~ 5 K above the zero field T_C are compared in Fig. 3. With increasing magnetic field, resistance drops sharply around 20 kOe, rapidly approaching saturation. With decreasing magnetic field, MR jumps back to zero with a ~ 5 kOe hysteresis between the magnetic-field increasing and the decreasing branches. The starting point for each measurement is in the high resistance monoclinic (MC) paramagnetic (PM) phase, and, therefore, it is driven into the low resistance FM orthorhombic (OR) phase by magnetic fields exceeding temperature-specific critical values. Conversely, the magnetic-field-induced FM OR phase transforms back into the PM MC phase with decreasing magnetic field. Consistent with the temperature dependent data, the magnetic-field dependence of the MR ratio is also anisotropic: the largest negative values are -24% , -21% , and -14.5% along the [100], [010], and [001] directions, respectively.

In order to obtain further insight into the nature of the observed MR behavior, electronic structure and diffusion

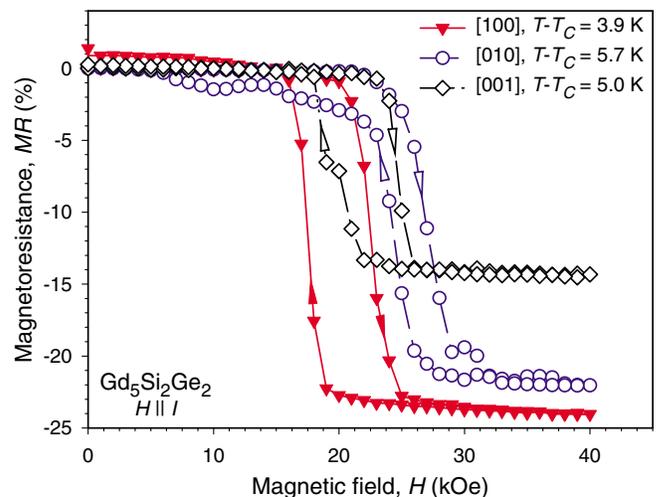


FIG. 3 (color online). The magnetic-field dependencies of the MR ratios of $Gd_5Si_2Ge_2$ along the [100], [010], and [001] crystallographic directions measured ~ 4 to ~ 6 K above the zero-field T_C 's.

conductivity of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ were calculated using the tight binding linear muffin-tin orbital (TB LMTO) method within local spin density approximation with the U correction approach (LSDA + U) for more accurate treatment of the $4f$ states of Gd atoms. The values of U (Coulomb repulsion between localized $4f$ electrons) and J (exchange interaction between localized $4f$ electrons) are equal to 6.7 and 0.7 eV, respectively [21]. To imitate disordering effects, two possible distributions of Si and Ge atoms in the unit cell were considered [called direct and inverse hereafter (see Ref. [10] for details)]. A mesh of 4800 \mathbf{k} points in the full Brillouin zone was sufficient to reach a few percent accuracy in the calculated conductivity tensor. Assuming that the MR effect is caused by the magnetic-field-induced MC \rightarrow OR phase transition and the concurrent modification of the electronic structure, we implement the following expression $\text{MR}_\alpha = (\sigma_{\text{MC}}^{\alpha\alpha} - \sigma_{\text{OR}}^{\alpha\alpha})/\sigma_{\text{OR}}^{\alpha\alpha} \times 100\%$, where α corresponds to Cartesian coordinates and $\sigma_{\text{OR}}^{\alpha\alpha}$ and $\sigma_{\text{MC}}^{\alpha\alpha}$ are diffusion conductivity tensors of the OR and MC phases, respectively, which were calculated in the relaxation time approach [22]

$$\sigma_{\alpha\alpha} \propto \tau \sum_{\mathbf{k}, \nu, s} v_{\nu, s}^\alpha(\mathbf{k}) v_{\nu, s}^\alpha(\mathbf{k}) \delta[\varepsilon_{\nu, s}(\mathbf{k}) - E_F] \equiv \tau \langle v^\alpha v^\alpha \rangle. \quad (1)$$

In Eq. (1), τ is the relaxation time, $\mathbf{v}_{\nu, s} = \partial \varepsilon_{\nu, s}(\mathbf{k})/\partial \mathbf{k}$ is the electronic group velocity, $\varepsilon_{\nu, s}(\mathbf{k})$ is the energy spectrum, and \mathbf{k} , ν , and s are the wave vector, band, and spin indices, respectively. We calculated electronic velocity for FM ordering in the OR phase and FM and antiferromagnetic (AFM) orderings in the MC phase.

The results of theoretical calculations are presented in Table I and Fig. 4. MR ratios are in qualitative agreement with the experimental data regardless of the magnetic order in the high-temperature phase. In the case of the

TABLE I. Calculated values of $\langle v_a^2 \rangle$ at E_F . In OR and MC phases, direct and inverse configurations of Ge and Si atoms and two types of magnetic order in MC phase (FM and AFM) were considered. All values are normalized to $\langle v_{[100]}^2 \rangle$ in the OR phase with direct configuration. $\Delta \langle v_a^2 \rangle = \langle v_a^2 \rangle(\text{MC-FM or MC-AFM}) - \langle v_a^2 \rangle(\text{OR-FM})$ and $\text{MR} = \Delta \langle v_a^2 \rangle / \langle v_a^2 \rangle(\text{OR-FM}) \times 100\%$ for different directions and two types of magnetic orderings in the MC phase are shown.

Configuration	α	$\langle v_a^2 \rangle$		$\Delta \langle v_a^2 \rangle$		MR(%)	
		OR-FM	OR-FM	MC-FM	MC-AFM	MC-FM	MC-AFM
Direct	[100]	1.00	-0.20	-0.61	-20	-61	
	[010]	0.54	-0.18	-0.38	-33	-70	
	[001]	0.96	-0.18	-0.23	-19	-24	
Inverse	[100]	0.92	-0.29	-0.56	-32	-61	
	[010]	0.51	-0.18	-0.31	-35	-61	
	[001]	0.81	-0.15	0.01	-19	0	

AFM ordering of the MC phase, the MR is overestimated by more than a factor of 2, yet it still demonstrates the same anisotropy. The larger MR ratios for the case of AFM ordering of the MC phase are related to a sharp peak in the density of states (DOS) at the Fermi energy (E_F) corresponding to d states of Gd atoms with a very small dispersion of $\varepsilon(\mathbf{k})$ at E_F . Therefore, AFM ordering will not be considered in the following discussion.

The $\sim 30\%$ increase of the $T1B$ - $T1B$ (see notations in Ref. [7]) distance in the MC phase [6–8] leads to a natural decrease of Si(Ge)-Si(Ge) interactions [7,10]. This weakening of bond strength reduces splitting between corresponding bonding and antibonding states. As a result, the position of the antibonding p states is lowered in the MC phase as indicated by large peaks below E_F at -1.1 and -0.65 eV for the majority (Fig. 4) and -0.5 and -0.1 eV for the minority (not shown) spin states in the DOS of $T1B$ atoms. The $T1A$ - $T1A$ distance does not change through the transition [6–8] and the DOS of $T1A$ atoms (Fig. 4) varies insignificantly. A shift of the antibonding states becomes apparent as a significantly decreased dispersion of bands 1, 5, and 6 that occurs in the MC phase. Reduced dispersion of band 1 is responsible for the peak at -0.65 eV in the DOS of the MC phase, and it leads to the corresponding reduction of $|\mathbf{v}(\mathbf{k})|$ at the Fermi level.

The main contribution to electrical conductivity corresponds to d electrons of Gd atoms, while Ge and Si atoms are responsible for about 20% of its total value. Our calculations demonstrate that absolute change of $\langle v_a^2 \rangle$ is practically the same for the [010] and [001] directions in the direct configuration and slightly smaller for the [001] direction in the inverse configuration (see Table I). This

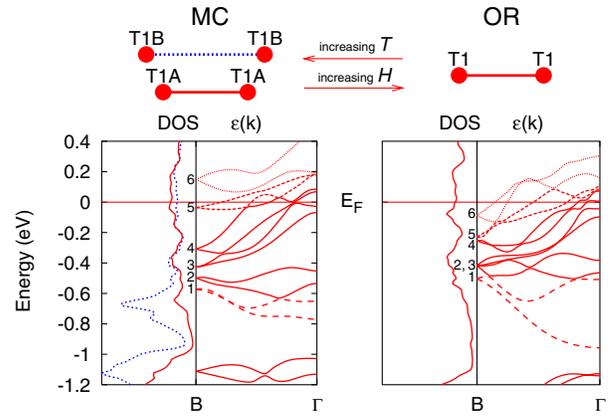


FIG. 4 (color online). The most relevant bands in the electronic structure of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ modified through magnetostructural phase transition showing the DOS of the $T1$ atoms (solid line, right-hand side) in the OR phase; the $T1A$ (solid line) and the $T1B$ (dashed line) in the MC phase and the band structure along the [100] direction for majority spin states. E_F corresponds to zero energy. The short $T1$ - $T1$ bond in the OR phase splits into two different bonds in the MC phase: the short $T1A$ - $T1A$ bond and the elongated by $\sim 30\%$ $T1B$ - $T1B$ bond.

result correlates with the almost negligible change of interatomic distances along these two crystallographic directions through the structural transition and the reduction of conductivity occurs because of the increased $T1B$ - $T1B$ distance. A larger MR ratio in the [010] direction (perpendicular to the slabs) arises from the smaller $\langle v_{[010]}^2 \rangle$ value compared to the in-slab [100] and [001] directions; see Table I. As is well documented for this series of compounds [7,8,13], the slabs that could be treated as infinite along the [100] and [001] directions are stacked along the [010] direction, and they may or may not be connected by Si(Ge)-Si(Ge) covalent bonds through Si(Ge) located at $T1B$ sites. The most dramatic structural changes occur along the [100] direction, and certain interactions along the [010] direction alternatively break and reform through breaking and reforming of the interslab Si(Ge)-Si(Ge) bonds. Owing to the significant distortion occurring between the slabs along the [100] direction but almost ignorable interatomic distances variability along [010] and [001] [7,8,13], the conductivity along the [100] direction is reduced more profoundly (see $\Delta\langle v_{[100]}^2 \rangle$ in Table I), and the MR ratio is -20% and -32% in the direct and inverse configurations, respectively. A large MR in the [100] direction in the inverse configuration is related to a large contribution to the DOS at the Fermi level from Si atoms in $T1B$ positions, rather than from $T1B$ Ge atoms. As a result, the change of electronic velocity at E_F caused by the above-described modification of the antibonding states of $T1B$ sites is more significant for Si atoms. Correspondingly, the values of the MR ratio statistically averaged over direct and inverse configurations are -26% , -34% , and -19% in the [100], [010], and [001] directions, respectively. This result is in agreement with the experimental data.

In summary, the MR of a $Gd_5Si_2Ge_2$ single crystal has been studied both experimentally and theoretically as a function of crystallographic direction, magnetic field, and temperature. The MR ratio of up to -25% is observed around the T_C with a 20 kOe magnetic field applied along the [100] and [010] directions, which is higher than the -14% observed along the [001] direction. The MR effect calculated from electrical conductivity values along different directions is in qualitative agreement with the experiment. Theoretical calculations indicate that the MR ratio shows some dependence on the type of magnetic order in the high-temperature phase, but the anisotropy of MR does not. The anisotropy of the MR in $Gd_5Si_2Ge_2$ arises from a structural transition taking place concur-

rently with a ferromagnetic ordering at T_C because, first, drastic changes in the lattice occur along the [100] direction and, second, interactions between the slabs along the [010] direction are greatly affected by variability of $T1B$ - $T1B$, Gd-Gd, and Gd-Si(Ge) interslab bonds. Combined, these changes in this layered crystal structure result in the largest MR along the [100] and [010] directions, while the MR along the [001] direction is the smallest.

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