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Spontaneous generation of voltage in the magnetocaloric compound $Tb_5Si_{2.2}Ge_{1.8}$ and elemental Gd

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ABSTRACT

The spontaneous generation of voltage (SGV) in single crystalline $Tb_5Si_{2.2}Ge_{1.8}$ and Gd has been studied. Temperature-induced SGVs were observed along the three principal crystallographic axes of $Tb_5Si_{2.2}Ge_{1.8}$, but not in Gd. Field-induced SGVs were observed with magnetic fields less than 40 kOe applied along the *a*-axis of $Tb_5Si_{2.2}Ge_{1.8}$, and the *c*-axis of Gd. The absence of the temperature-induced SGV in Gd indicates the key role first-order phase transformations play in the appearance of the effect when temperature varies. The anisotropy of the magnetic field-induced SGV in $Tb_5Si_{2.2}Ge_{1.8}$ and the existence of the field-induced SGV in Gd, highlight the importance of the magnetocaloric effect in bringing about the SGV.

1. Introduction

Interesting physical properties, such as the giant magnetocaloric effect (GMCE), giant magnetoresistance (GMR), colossal magnetostriction, and spontaneous generation of voltage (SGV) [1–3] are known to occur in rare earth intermetallic compounds $R_5(Si_xGe_{1-x})_4$, where R is a lanthanide element. All of these effects originate from first-order coupled magnetic and crystallographic phase transformations when R = Gd [1]. When $0 < x \leq 0.3$, the phase transformation is between a ferromagnetic orthorhombic phase [O(I)/FM] and a different orthorhombic phase in its antiferromagnetic state [O(II)/AFM]. When $0.4 < x \leq 0.503$, the transformation is between a ferromagnetic orthorhombic phase [O(I)/FM] and a paramagnetic monoclinic phase [M/PM]. Temperature, magnetic field, and/or pressure have been identified as triggers of these transformations [1,4].

Different from $Gd_5(Si_xGe_{1-x})_4$, the magnetic and crystallographic phase transformations of $Tb_5(Si_xGe_{1-x})_4$ between O(I)/FM and M/PM are decoupled by ∼10 K and less than 5 K when $x = 0.5$ and 0.55, respectively [5–7]. These independent magnetic and crystallographic phase transformations can be recoupled by applying moderate hydrostatic pressures and/or magnetic fields as has been demonstrated for a polycrystalline sample with $x = 0.5$ and a single crystal with $x = 0.55$ [6,8]. The recoupling results in a 40% enhancement of the GMCE in polycrystalline $Tb_5Si_2Ge_2$ ($x = 0.5$) [8]. It is worth noting that in a single crystal of $Tb_5Si_{2.2}Ge_{1.8}$ ($x = 0.55$), the GMCE only occurs when the magnetic field is applied parallel to the *a*- and *c*-axes [6]. Interplay between decoupling and recoupling of the magnetic and structural transformations indicates a complex energy landscape separating different magnetic and crystallographic phases, and the complexity is enhanced by the single ion anisotropy of Tb^{3+} when compared to $R = Gd^{3+}$ [6].

The SGV has been observed in both polycrystalline and single crystalline $Gd_5(Si_xGe_{1-x})_4$ in the vicinity of the Curie temperature (T_C) when either temperature was varied at constant field or when magnetic field was changed isothermally [2,3]. The origin of SGV in these compounds is believed to be thermoelectric power, i.e., Seebeck effect [2,3]. Because a small compositional difference is always present between the two ends of a sample and because small temperature gradients are always present across a sample when its temperature is actively controlled, phase transformation typically starts at one end of the specimen and then propagates to the other. The heat release or absorption during this process gives rise to measurable temperature gradients necessary for the generation of the thermoelectric signal.

The study of SGV in $Tb_5(Si_xGe_{1-x})_4$ compounds is a continuation of previous studies of $Gd_5(Si_xGe_{1-x})_4$ [2,3]. To gain a better understanding of the role that different factors play in the appearance of the SGV, a single crystal of Gd metal has also been examined with respect to both temperature and magnetic field-induced spontaneous voltage. Among the materials undergoing second order magnetic order–disorder transformations, elemental Gd has one

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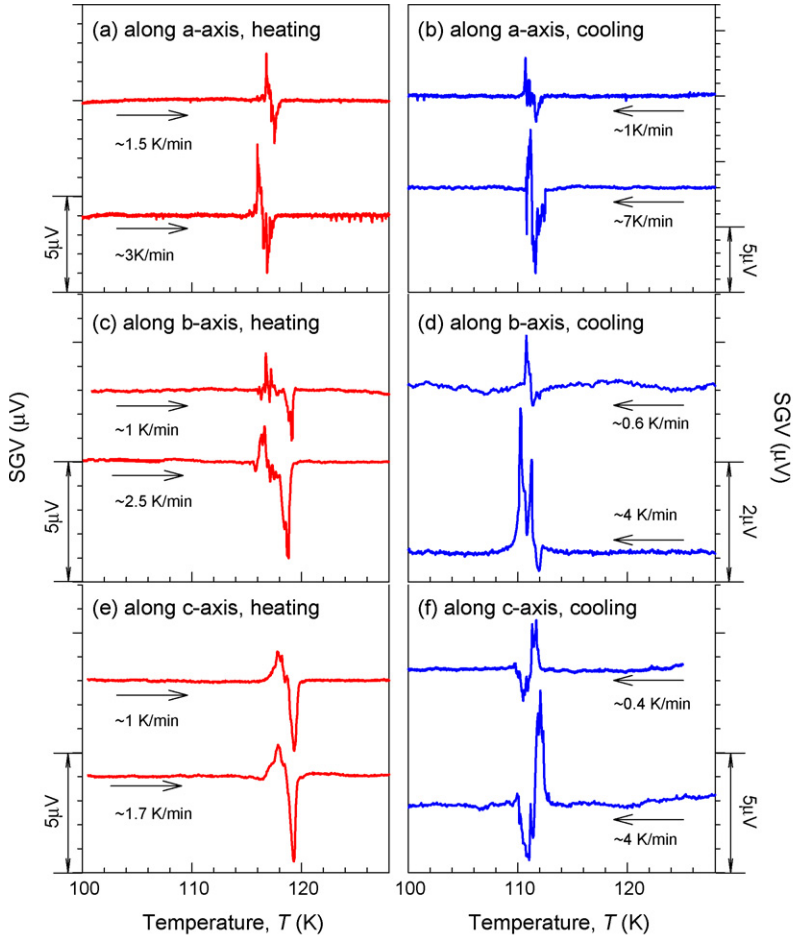

Fig. 1. The SGV of $Tb_5Si_{2.2}Ge_{1.8}$ as a function of temperature measured along the *a*-, *b*-, and *c*-axes upon heating and cooling at various rates in a zero magnetic field.

of the highest MCE's around room temperature, which is about half that observed in $Gd_5(Si_xGe_{1-x})_4$ [9]. A small anisotropy due to dipolar and spin–orbit couplings results in the *c*-axis of Gd being the magnetic easy axis immediately below $T_C = 293$ K [10,11].

2. Experimental

Two $Tb_5Si_{2.2}Ge_{1.8}$ single crystals were grown by the tri-arc method [12] from high purity Tb, Si and Ge mixed in the appropriate stoichiometry. The two Tb stocks [99.67 at.% (99.97 wt.%) and 99.89 at.% (99.99 wt.%) pure with respect to all other elements in the periodic table] were prepared by the Materials Preparation Center (MPC) of the Ames Laboratory [13]. The Si and Ge were purchased from commercial vendors, and were better than 99.999 wt.% pure. The as-grown crystals were oriented by using backscatter Laue X-ray diffraction.

Three rectangular parallelepiped samples were cut by spark erosion. They were 5.03 mm × 0.98 mm × 0.44 mm, 3.38 mm × 0.94 mm × 0.57 mm, and 4.66 mm × 1.02 mm × 0.82 mm with the longest dimensions of each along the *a*-, *b*-, and *c*-axes, respectively. The *a*- and *b*-axes samples came from the single crystal prepared using 99.67 at.% pure Tb metal, and the *c*-axis sample came from the 99.89 at.% pure Tb. Four thin platinum wires were attached to each sample with H20E Epotek silver epoxy manufactured by Epoxy Technology. The samples were also used for an electrical resistivity study, results of which will be published elsewhere. The distances between the voltage contacts were 1.20, 1.14, and 3.03 mm for the *a*-, *b*-, and *c*-axes samples, respectively. Typical contact resistances of the freshly prepared samples were between 1 and 2 Ω.

The single crystal Gd was prepared using the strain-anneal method from polycrystalline Gd metal also prepared by the MPC. The metal was 99.89 at.% (99.98 wt.%) pure with respect to all other elements in the periodic table. A rectangular parallelepiped sample was cut using the spark erosion technique from a large grain. Its dimensions were 9.12 mm × 3.02 mm × 1.21 mm with the longest side along the *c*-axis. Four thin platinum wires were attached to the sample by using a spot welding technique. The distance between the voltage contacts was 7.60 mm. Contact resistance of the freshly prepared samples was below 1 Ω. The SGV measuring method, instrument set up, and experiment errors were described elsewhere [3].

3. Results and discussion

As shown in Fig. 1, temperature-induced SGV appears along all three major crystal axes of $Tb_5Si_{2.2}Ge_{1.8}$ between 110 and 118 K, where the crystallographic and magnetic phase transformations occur [6,7]. The SGV starting temperatures are different upon heating and cooling by ~5 K. This separation is nearly the same as the extent of thermal hysteresis of the crystallographic phase transformation [6]. Therefore, one can associate the SGV with the crystallographic transformation. Fig. 1 also shows that the SGV increases with the increased rate of temperature change, which is similar to that observed in $Gd_5Si_2Ge_2$ [3]. On the other hand, a magnetic field of 40 kOe and lower can trigger the SGV only when the field vector is parallel to the *a*-axis. A representative result at 120 K is displayed in Fig. 2. This observation is different from $Gd_5Si_2Ge_2$, where the SGV occurs when a magnetic field is isothermally applied along any of the three major crystallographic directions in the vicinity of T_C [3].

Both neutron and X-ray powder diffraction studies of $Tb_5Si_{2.2}Ge_{1.8}$ illustrate a temperature-induced first-order crystallographic phase transformation involving a large unit cell volume change of ~1% [6,7]. By rearranging the Clausius–Clapeyron equation [14] $(dP/dT) = (\Delta S/\Delta V) = (\Delta E/T\Delta V)$ to $\Delta E = T(dP/dT)\Delta V$, where *P*, *T*, *S*, *V*, and *E* are the pressure, temperature, entropy, volume, and enthalpy, respectively, it is obvious that the enthalpy change,

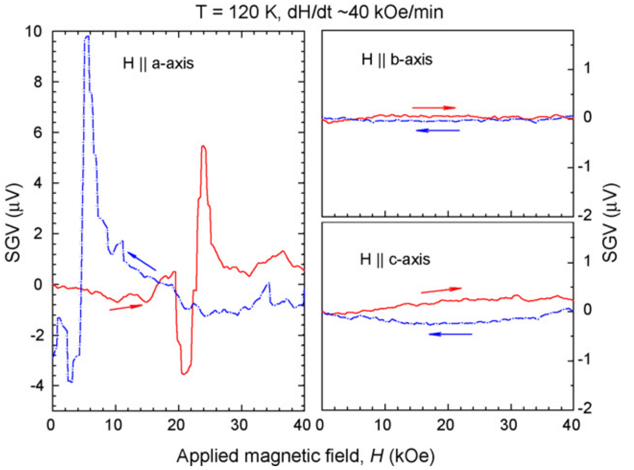

Fig. 2. The SGV of $Tb_5Si_{2.2}Ge_{1.8}$ as a function of magnetic field applied along the *a*-, *b*-, and *c*-axes at 120 K. The field change rate is ~40 kOe/min. The arrows mark the directions of the magnetic field changes.

i.e., latent heat, is proportional to the unit cell volume change. The latent heat in turn determines the temperature gradient across the sample when its crystallographic phase transformation starts from one end of the specimen and then propagates to another. Since temperature is a scalar, the appearance of SGV does not depend on the orientations of the samples. Therefore, temperature-induced SGV appears along all three major crystal axes, and depends on the latent heat of the first-order phase transformation.

The anisotropy of the magnetic field-induced SGV in $Tb_5Si_{2.2}Ge_{1.8}$ is in line with its highly anisotropic metamagnetism and magnetocaloric effect (MCE) [6]. Both the PM ↔ FM metamagnetism and GMCE occur only with $\mathbf{H}||\mathbf{a}$ when $H \leq 40$ kOe [6]. The absence of SGV with $\mathbf{H}||\mathbf{b}$ and $\mathbf{H}||\mathbf{c}$ when $H \leq 40$ kOe (Fig. 2) confirms that it is the magnetocaloric effect that is responsible for the temperature gradients necessary for the observation of the field-induced SGV.

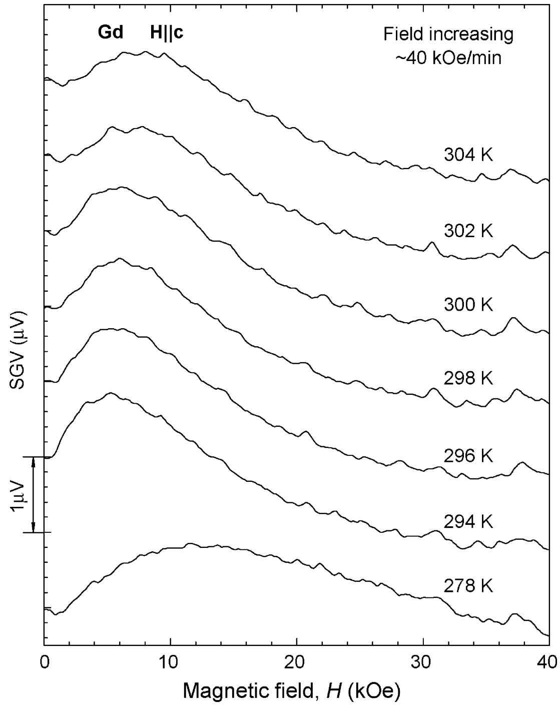

Fig. 3. The SGV of Gd as a function of magnetic field applied along the *c*-axis at constant temperatures between 278 and 304 K. The measurements were carried out with field increasing at a rate of ~40 kOe/min.

The roles played by latent heat and MCE in SGV were further studied by using a single crystal of Gd metal. No SGV occurs in the vicinity of $T_C = 293$ K as long as the magnetic field remains constant. Since the phase transition at T_C is a pure second order magnetic one, no latent heat is involved here. The absence of SGV in the elemental Gd near T_C supports the notion that the temperature-induced SGV depends on the latent heat of the first-order phase transformation.

The SGV in Gd can be triggered by applying a magnetic field isothermally in the vicinity of T_C. Fig. 3 exhibits the SGV of Gd as a function of magnetic field applied along the *c*-axis between 278 and 304 K with a field increasing at the rate of ~40 kOe/min. The largest magnitude of SGV, which is taken as the voltage difference between the positive and negative peaks, is ~2 μV. It is observed at 294 K, i.e., in the immediate vicinity of the maximum MCE, which occurs at 293 K. This is much smaller than the SGV of $Gd_5Si_2Ge_2$ [3] and $Tb_5Si_{2.2}Ge_{1.8}$ single crystals (see Fig. 2). Consistent with the behavior of the MCE in Gd, which decreases gradually as the temperature is further and further away from T_C, (see Ref. [15]), the magnitude of the SGV signal exhibits a similar reduction with temperature as is clearly seen in Fig. 3. Furthermore, since the thermoelectric signal is proportional to the temperature difference (ΔT) between two ends of a specimen, and $Gd_5Si_2Ge_2$ and $Tb_5Si_{2.2}Ge_{1.8}$ have a greater MCE compared to that of Gd, one concludes that the MCE determines ΔT, and therefore, determines the magnitude of the magnetic field-induced SGV.

4. Conclusions

Temperature-induced SGV has been observed in $Tb_5Si_{2.2}Ge_{1.8}$ along three major crystallographic axes near T_C, but not in a Gd single crystal. This suggests that a phase transformation involving a large volume change, i.e., a large latent heat, is necessary for the temperature-induced SGV. The magnetic field-induced SGV has been observed in $Tb_5Si_{2.2}Ge_{1.8}$ near T_C only with $\mathbf{H}||\mathbf{a}$, but not with $\mathbf{H}||\mathbf{b}$ and $\mathbf{H}||\mathbf{c}$ when $H \leq 40$ kOe. The field-induced SGV has also been observed in Gd near T_C. These observations indicate that a first-order magnetostructural phase transformation is not a necessary condition for SGV to occur. But a large MCE for the magnetic field-induced SGV is necessary for the latter in order to be observed.

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