Random magnetic anisotropy in a new compound Sm$_2$AgSi$_3$

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We report the experimental study on the structural and magnetic properties of a new ternary intermetallic compound Sm$_2$AgSi$_3$. The properties of the sample were investigated in detail by X-ray diffraction, dc–magnetization, and heat capacity measurements. The polycrystalline compound of Sm$_2$AgSi$_3$ crystallizes in the ThSi$_2$-type tetragonal structure (space group $I_4/mmd$). The temperature–dependent dc–magnetization and heat capacity results demonstrate that the compound undergoes ferromagnetic behaviour with a Curie temperature ($T_C$) of 14 K. The large coercive field in hysteresis loops and the thermomagnetic irreversibility in the ferromagnetic region revealed that the compound exhibits a large magnetic anisotropy. The magnitude of the applied field and the coercivity obtained from the M-H loops corroborate with the thermomagnetic irreversibility in the magnetization data. The magnetic contribution of the heat capacity reveals a broad Schottky–type anomaly above $T_C$, due to the presence of the crystal electric field effect of Sm$^{3+}$ in Sm$_2$AgSi$_3$.

Keywords: Ferromagnet; Magnetic anisotropy; Thermomagnetic irreversibility; Schottky peak.

The ternary intermetallic compounds R$_2$TX$_3$ ($R =$ rare earths, $T =$ transition metals, $X =$ Si, Ge, Al, and In), are extensively studied for their structural and magnetic properties. Most of the compounds with R$_2$TX$_3$ stoichiometry form in ThSi$_2$ type both hexagonal and tetragonal crystal structure. The magnetic R ions occupy the Th position, while the T and X ions mutually occupy the Si positions in ThSi$_2$. Recently, the random magnetic anisotropy in a polycrystalline ThSi$_2$ type hexagonal compound Sm$_2$NiSi$_3$ was confirmed from the temperature dependence of zero-field cooled (ZFC) and field-cooled (FC) magnetization and magnetic entropy changes.

Samarium (Sm) based intermetallic compounds have gained considerable interest because of their interesting properties such as superconductivity, magneto–resistance, magnetic and non magnetic behaviour. Sm based ternary and binary compounds can show large magnetic hysteresis due to their large magnetic anisotropy and may be used as a permanent magnet. A strong magneto-crystalline anisotropy may be produced by Sm$^{3+}$ ion as a consequence of the crystal electric field (CEF) effect acting on the 4f-electrons.

In recent years, the development of magnetic materials has posed a great challenge to researchers. To the best of our knowledge, the existence of Sm$_2$AgSi$_3$ compound was not earlier reported. In this work, we have reported the detailed synthesis process and magnetic properties of a new compound Sm$_2$AgSi$_3$. The large random magnetic anisotropy in Sm$_2$AgSi$_3$ is also demonstrated.

A. Experimental Set-up

A polycrystalline sample Sm$_2$AgSi$_3$ was prepared under ultra-high purity argon atmosphere using the standard arc-melting technique. The melted ingot was turned over and remelted five times to ensure a good homogeneity. The melted sample was wrapped in a tantalum foil and sealed in a vacuum quartz tube. The tube was kept in a furnace for annealing at 1373 K for one week and then quenched in cold water. The sample was characterized by powder X-ray diffraction (XRD) using CuK$_\alpha$ radiation of a Rigaku XRD machine. The Rietveld analysis of XRD patterns was carried out using FULLPROF software. The temperature and field dependence of dc–magnetization measurement was performed using a Dynacool physical properties measurement system (PPMS) made by Quantum Design, USA. Heat capacity measurements were carried out using the same equipment.

B. Results and Discussion

1. X-ray Diffraction

Fig. 1 shows the room-temperature powder XRD pattern along with the Rietveld refinement fitting profile of polycrystalline Sm$_2$AgSi$_3$. The Rietveld refinement result reveals that the compound form in a $\beta$–ThSi$_2$–type of tetragonal structure with space group $I_4/mmd$. The crystallographic parameters from the refinement are listed in Table I. The inset of Fig. 1 shows the schematic diagram of the crystal structure of Sm$_2$AgSi$_3$. The shortest distance between Sm atoms is 4.119 Å, and is twice larger than the expected ionic radius of Sm$^{3+}$ ($r_{Sm} = 0.958$ Å). This suggests that there is a weak interaction between the rare–earth atoms in Sm$_2$AgSi$_3$.

2. Magnetic Properties

Fig. 2 shows the temperature dependence of ZFC and FC dc–magnetic susceptibility ($\chi(T)$) with an applied field ($H_{app}$) of 1 T. The dc–$\chi(T)$ shows a typical para-
The positive value of $\theta$ yielded the least-squares fit (LSQ) fit to the experimental data. The Curie constant, $\chi_0$, and the magnetic susceptibility which includes the core-electron diamagnetism was fitted on the Curie–Weiss law, $\chi = \frac{C}{T-\theta_P} + \chi_0$, (where $C$ is the Curie constant, $\theta_P$ is the Weiss paramagnetic temperature and $\chi_0$ is the temperature-independent magnetic susceptibility which includes the core-electron diamagnetism) was fitted on the $\chi(T)$ of Fig. 2 for $T > 20$ K. The least-squares fit (LSQ) fit to the experimental data yielded $\theta_P = 12$ K and $\chi_0 = 3.1 \times 10^{-4}$ emu/mole.Oe. The positive value of $\theta_P$ shows that the dominant interaction is ferromagnetic in Sm$_2$AgSi$_3$. The effective magnetic moment ($\mu_{eff}$) value was calculated from the fitting parameter value of C and found to be $0.57 \mu_B$/Sm$^{3+}$. A small deviation of $\mu_{eff}$ from the theoretical value of free ion Sm$^{3+}$ [$g\sqrt{J(J+1)} = 0.85 \mu_B$] may arise from crystal field effects (CEF). The expanded region in low temperature of $\chi(T)$ for different magnetic fields shows the inset of Fig. 2. As seen in the inset, there is a thermal magnetic irreversibility (TMI) shown between the data collected in the ZFC and FC protocols. The TMI point is defined as the temperature at which the $\chi_{ZFC}$ and $\chi_{FC}$ curves bifurcate from each other. It is also observed that TMI depends on the $H_{app}$. It can be believed that the large magnetic anisotropy may cause the TMI behavior in $\chi(T)$ for high $H_{app}$. Fig. 3 shows the field-dependent magnetization $M(H)$ loops at different temperatures. The well-defined hysteresis below $T_C$ is observed in the ferromagnetic ordered region of Sm$_2$AgSi$_3$. The $M(H)$ loops do not saturate even at a high field value of 9 T at 2 K. The spontaneous magnetization was calculated from $M(H)$ at 2 K, and the obtained value is $0.25 \mu_B$/Sm. This value is smaller by a considerable margin than the expected saturation moment value for parallel alignment of Sm$^{3+}$ spin ($gJ = 0.71 \mu_B$, with $g = 2/7$, and $J = 5/2$). The low magnetization value is attributed to the influence of the magnetic anisotropy in saturation. As seen in the M-H loops, a large value of coercivity ($H_C$) of 0.8 T at 2 K appears for a polycrystalline rare-earth based compound. This large $H_C$ may result from the random magnetic anisotropy of the sample. For more details, the $M(H)$ loops were measured at different temperatures. The $H_C(T)$ and remanence magnetization was estimated from $M(H)$ loops.

**FIG. 1.** X-ray powder diffraction data for Sm$_2$AgSi$_3$. Red symbols represent the experimental data and the black line represents the calculated data. The difference between experimental and calculated data is shown as a blue line. A set of vertical bars represents the Bragg peak positions of the tetragonal $\alpha$-ThSi$_2$ type structure. Inset: The schematic representation of the tetragonal crystal structure of Sm$_2$AgSi$_3$. The blue balls are for Sm and silver–red color balls are for Ag+Si.

| Atom | Wyckoff | x   | y   | z   |
|------|---------|-----|-----|-----|
| Sm   | 4a      | 0   | 3/4 | 1/8 |
| Ag   | 8c      | 0   | 1/4 | 0.2895(2) |
| Si   | 8c      | 0   | 1/4 | 0.2895(2) |

**TABLE I.** The lattice parameters, unit cell volume and the atomic coordinate positions of Sm$_2$AgSi$_3$ obtained from the Rietveld refinement of XRD patterns. The refinement quality parameter is $\chi^2 = 5.7$.

$\alpha = b = 4.128(2)$ Å

$c = 14.254(2)$ Å

$V = 242.890(1)$ Å$^3$

FIG. 2. Temperature dependence of the field-cooled (FC) and zero-field-cooled (ZFC) dc–magnetic susceptibility ($\chi(T)$) at 1 T of Sm$_2$AgSi$_3$ along with a fit to the data (green line) of a modified Curie-Weiss law. Inset shows ZFC and FC of $\chi(T)$ at low temperature region for various applied magnetic fields.
for each temperature and found to gradually decrease with increasing temperature. The temperature variation $H_C(T)$ is plotted in inset (a) of Fig. 3. An exponential behavior described by the relation $H_C(T) = A e^{B T}$ is observed. The fitting is shown as a blue line on the data. The best fitting parameters obtained from the $H_C(T)$ vs. $T$ curve are $A = 1.256$ T and $B = 0.234$ K$^{-1}$ represent the $H_C$ at 0 K and the steep temperature respectively. The steep temperature dependence of $H_C(T)$ in ferromagnet suggests that the observed hysteresis of Sm$_2$AgSi$_3$ is appropriate for large magnetic anisotropy.

The magneto–crystalline anisotropy constant of magnetic materials are evaluated from the law of approach to saturation. The law of approach to saturation is therefore applied on the $M(H)$ by fitting Eq. 1 on the high magnetic field magnetization data as

$$M = M_S \left[ 1 - \frac{D}{H^2} \right] + \chi_0 H^{1/2},$$

where $M_S$ (in A/m) is the saturation magnetization. Here, $D$ is a function of magnetic anisotropy energy and $\chi_0 H^{1/2}$ denotes the term related to para-process. The parameter $D$ is expressed as:

$$D = \frac{8}{15} \frac{K_1^2}{\mu_0^2 M_S^2} (\text{A/m})^2,$$

where $K_1$ is the anisotropy constant in J.m$^{-3}$ and $\mu_0$ is the free space magnetic permeability. For polycrystalline material, it is assumed that the overall possible orientations of the individual crystallites are averaged.

The value of $K_1$ was estimated by using the fitting parameters $B$ and $M_S$ on Eq. 2. The obtained $K_1$ value is $|K_1| = 1.3 \times 10^5$ J.m$^{-3}$ at 2 K. The obtained value of $|K_1|$ is comparable with $9.2 \times 10^6$ J.m$^{-3}$ for SmFe$_3$Ti and $4.0 \times 10^6$ J.m$^{-3}$ for Sm$_3$Fe$_2$O$_{12}$.[27] The observed large hysteresis loop in $M(H)$ and comparable value of $|K_1|$ revealed that a random magnetic anisotropy exists in Sm$_2$AgSi$_3$.

The anisotropy field plays a crucial role in determining the FC magnetic susceptibilities ($\chi_{FC}$) and the ZFC magnetic susceptibilities ($\chi_{ZFC}$) at a given field value. The temperature variation of anisotropy field and $H_{app}$ for measuring $\chi(T)$ plays a major role in determining the degree of TM. Joy et al.[13,20] have proposed an empirical relation between $H_{app}$, $H_C$, $\chi_{FC}$ and $\chi_{ZFC}$ for a ferromagnetic system:

$$\chi_{ZFC} = \chi_{FC} \frac{H_{app}}{H_{app} + H_C},$$

This Eq. 3 indicates that the $\chi_{ZFC}$ and $\chi_{FC}$ should overlap in that temperature regime for $H_{app} \gg H_C$. However, the difference between the $\chi_{ZFC}$ and $\chi_{FC}$ values is large for $H_{app} \ll H_C$. Hence, it can be assume that the hysteresis between $\chi_{ZFC}$ and $\chi_{FC}$ arises even at high field $H_{app}$ of 1.0 T due to the magnetic anisotropy in the sample. However, the $\chi_{ZFC}$ for $H = 0.5$ T starting from negative values of at low temperatures is due to this anisotropic sample being cooled in a net negative trapping field. This trap magnetic field commonly exists in the PPMS superconducting solenoid magnet.[21]

3. Heat Capacity

The temperature variation of heat capacity ($C_p(T)$) of Sm$_2$AgSi$_3$ and of the isostructural non–magnetic compound La$_2$AgSi$_3$ are depicted in Fig. 4. A value of $147$ J/(mol.–K) is attained at 300 K, very closed to the Dulong–Petit limit $3nR = 149.65$ J/(mol.–K) ($n = 6$ is the number of atoms per formula unit, $R$ stands for the gas constant). At low temperatures, $C_p(T)$ exhibits an anomaly in Sm$_2$AgSi$_3$ for the characteristic of a magnetic phase transition. The transition temperature of ~13 K is defined from the peak of $C_p(T)$, and is consistent with the $M(T)$ data.

The magnetic contribution of heat capacity ($C_{4f}$) for Sm$_2$AgSi$_3$ was estimated by subtracting the $C_p(T)$ data of La$_2$AgSi$_3$ from that of Sm$_2$AgSi$_3$ data and is shown in the inset of Fig. 4. As seen in the inset of Fig. 4 $C_{4f}(T)$ exhibits a broad hump above the transition temperature, indicating a Schottky type anomaly caused by crystalline electric field (CEF) present in this compound. The magnetic entropy $S_{4f}$ was estimated using the formula $S_{4f} = \int (C_{4f}/T) dT$. The temperature variation of $S_{4f}$ is shown in the right-hand axis of Fig. 4. The magnetic entropy is very close to Rln2 at $T_C$, indicating the
FIG. 4. (Left scale) Temperature dependence of zero field heat capacity ($C_P$) of La$_2$AgSi$_3$, and Sm$_2$AgSi$_3$. (Right scale) Temperature dependence of magnetic entropy of Sm$_2$AgSi$_3$. Inset: (left with bottom scale) temperature dependence for magnetic contribution of ($C_P$) for Sm$_2$AgSi$_3$ at low temperature region. (left with top scale) $T^{3/2}$ dependence of magnetic contribution of heat capacity for Sm$_2$AgSi$_3$.

presence of a doublet ground state in the magnetic system. $S_{4f}$ increases above $T_C$ and displays a tendency to saturate above 50 K. $S_{4f}$ saturates around a value of Rln6, indicating that the highest excited crystal field level contributes to magnetic entropy.

4. Summary

In this work the Sm$_2$AgSi$_3$ compound was synthesized and found to be stoichiometric and crystallizing in the $\beta$-ThSi$_2$-type tetragonal structure. The experimental results indicate that the compound undergoes a paramagnetic to ferromagnetic phase transition at $T_C = 14$ K. The large $H_C$ confirms that the compound possesses a large large anisotropy. The presence of magnetic anisotropy plays a role in the TMI between $\chi_{ZFC}$ and $\chi_{FC}$, and are related through $H_C$. The $C_M$ results indicate that the Schottky type anomaly is present due to the crystalline electric field (CEF), which may result in a large magnetic anisotropy. The present results pave the way for future promising research of magnetic properties in new R$_2$TX$_3$ series of compounds.

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