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Successive inverse and normal magnetocaloric effects in HoFeSi compound

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Magnetic properties and magnetocaloric effect (MCE) of HoFeSi compound have been studied systematically. HoFeSi compound undergoes two successive magnetic phase transitions with the variation of temperature: a paramagnetic to ferromagnetic (FM) transition around T_C =29 K followed by an FM to antiferromagnetic (AFM) or ferrimagnetic (FIM) transition at $T_t = 20$ K. The field dependence of magnetization reveals that a field-induced AFM/FIM-FM metamagnetic transition occurs below T_t with the increase in magnetic field. For a relatively low field change of 2 T, successive inverse and normal MCEs are observed and the maximum ΔS_M values reach as high as 5.6 and 7.1 J/kg K around T_t and T_C, respectively. This feature of successive inverse and normal MCEs in HoFeSi are suggested to be applied in some magnetic refrigerators with special designs and functions. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4865297]

I. INTRODUCTION

Nowadays, magnetic refrigeration based on the magnetocaloric effect (MCE) has been demonstrated as an alternative technology to conventional gas-cycle refrigeration for the applications in many aspects, such as domestic and industrial refrigeration around room temperature, specific applications in space science, and liquefaction of gas in low temperature region, etc.[1] The magnitude of MCE can be characterized by magnetic entropy change (ΔS_M) and/or adiabatic temperature change (ΔT_{ad}) when the material is exposed to a variation of magnetic field. Generally, the application of magnetic field will cause a reduction of magnetic entropy ($\Delta S_M < 0$), and then the magnetic material can be cooled by a subsequent adiabatic demagnetization. A great number of materials have been reported to exhibit large MCE around the transition from ferromagnetic (FM) to paramagnetic (PM) states.[2–5] However, recently some materials with first-order martensitic transition,[6,7] antiferromagnetic (AFM)-FM transition,[8,9] or ferrimagnetic (FIM)-FM transition[10,11] have been found to present inverse MCE ($\Delta S_M > 0$) when magnetic field is applied. These results open up another possible way to fulfill the magnetic refrigeration, that is, adiabatic magnetization rather than adiabatic demagnetization makes the sample to cool. Based on this concept, materials with inverse MCE are suggested to be utilized as "heat sinks" in composites with conventional MCE materials, so that they will enhance the efficiency of a refrigeration device.[6] Furthermore, the coexistence of normal and inverse MCEs has been observed in some materials with successive magnetic transitions, such as $NdBaMn_2O_6$ with normal MCE around PM-FM transition ($T_C = 290$ K) followed by inverse MCE near FM-AFM transition ($T_N = 210$ K).[8] Zhang *et al.* proposed a magnetic refrigerator using the materials with both inverse and normal MCEs, in which both magnetization and demagnetization processes are employed for cooling, and thus the efficiency of refrigeration can be improved largely.[12]

The rare earth (R)-based intermetallic compounds exhibiting large MCE have attracted much attention due to interesting magnetic properties as well as potential applications in magnetic refrigeration.[13–15] In 1970, Bodak *et al.* first reported the crystal structure of RFeSi compounds and they found that these materials crystallize in the tetragonal CeFeSi-type structure (space group $P4/nmm$), in which the Ce, Fe, and Si atoms occupy the crystallographic positions 2c [0.25, 0.25, $z_{Ce} = 0.672$], 2a [0.75, 0.25, 0], and 2c [0.25, 0.25, $z_{Si} = 0.175$], respectively.[16] Later, Welter *et al.* investigated the magnetic properties of RFeSi (R = La-Sm, Gd-Dy) compounds systematically by susceptibility measurements and neutron diffraction studies.[17] However, they did not report the magnetic properties of HoFeSi since the sample in their study was not sufficiently pure for the magnetic measurement. Recently, we studied the magnetic properties and MCE of ErFeSi compound, and found that ErFeSi exhibits a large reversible MCE around 22 K under relatively low magnetic field change (i.e., 2 T), suggesting that ErFeSi could be a promising material for magnetic refrigeration of hydrogen liquefaction.[18] In present work, we successfully

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synthesize pure HoFeSi compound with single phase, and further report the magnetic properties and MCE of HoFeSi compound.

II. EXPERIMENTAL DETAILS

The polycrystalline HoFeSi compound was prepared by arc-melting appropriate proportion of constituent components with the purity better than 99.9 wt. % in a water-cooled copper hearth under purified argon atmosphere. The ingot was re-melted several times with the button being turned over after each melting to ensure the compositional homogeneity. The obtained ingot was sealed in a high-vacuum quartz tube, annealed at 1373 K for 35 days, and then quenched into liquid nitrogen. Powder X-ray diffraction (XRD) measurement was performed at room temperature by using Cu $K\alpha$ radiation. The Rietveld refinement based on the XRD pattern was carried out to identify the crystal structure and the lattice parameters using the LHPM Rietica software.[19] Magnetizations were measured as functions of temperature and magnetic field by using a MPMS SQUID VSM magnetometer from Quantum Design, Inc.

III. RESULTS AND DISCUSSION

Figure 1 shows the powder XRD pattern of HoFeSi compound measured at ambient temperature and Rietveld refinement to the experimental data. The sample was detected to crystallize in a single phase with the tetragonal CeFeSi-type structure (space group *P*4/*nmm*). The lattice parameters *a* and *c* determined from the Rietveld refinement are 3.944(4) Å and 6.779(5) Å, respectively, which are consistent with the data in previous report.[16]

The temperature (T) dependences of zero-field-cooling (ZFC) and field-cooling (FC) magnetizations (M) for HoFeSi compound were measured under a magnetic field of 0.05 T as shown in Fig. 2(a). With the decrease in temperature, HoFeSi undergoes a PM-FM transition at the Curie temperatures (T_C) of 29 K. In addition, another anomaly around the

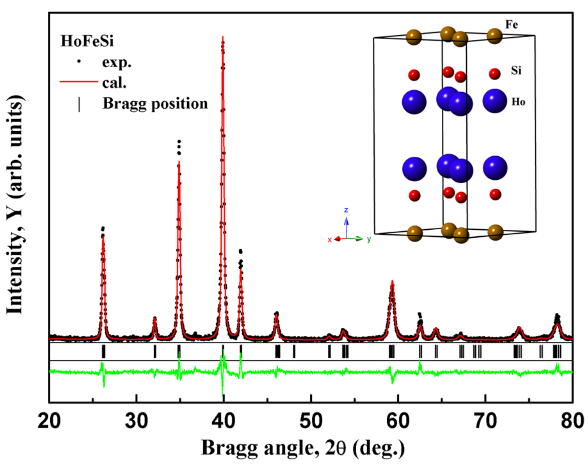

FIG. 1. The observed (dots) and calculated intensities (line drawn through the data points) of the fully refined X-ray diffraction pattern of HoFeSi compound at room temperature. The short vertical lines indicate the Bragg peak positions of the tetragonal CeFeSi-type structure. The lower curve shows the difference between the observed and calculated intensities. The inset shows the perspective view of the unit cell of HoFeSi.

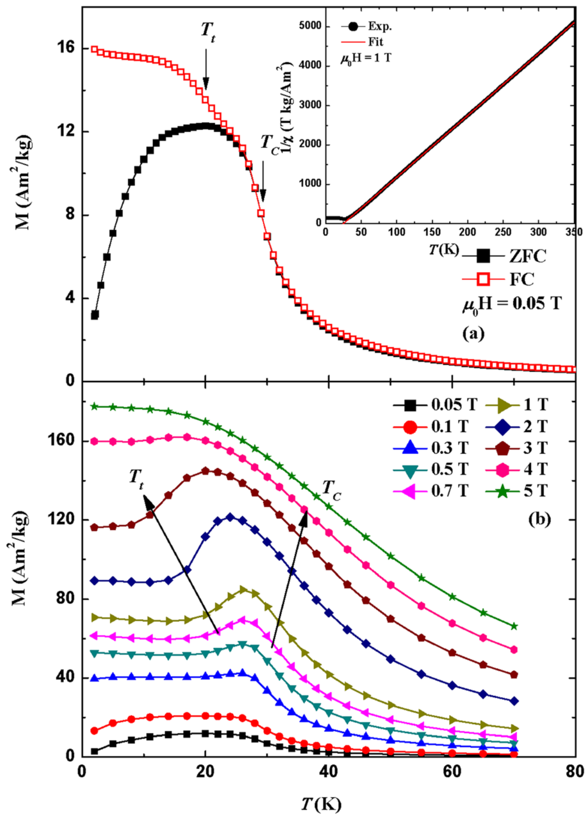

FIG. 2. (a) Temperature dependences of ZFC and FC magnetizations for HoFeSi under a magnetic field of 0.05 T. The inset shows the temperature dependence of inverse dc susceptibility (χ^{-1}) fitted to the Curie-Weiss law at 1 T in the temperature range of 2–350 K. (b) Temperature dependences of magnetization for HoFeSi in various magnetic fields.

transition temperature $T_t = 20$ K can be observed in FC curve. The analysis of magnetization isotherms (Fig. 3) indicates that HoFeSi may have a certain amount of AFM or FIM components at temperatures below T_t. Therefore, it is possible that part of magnetic moments in HoFeSi undergoes a FM-AFM/FIM transition around T_t, which leads to the less sharp change of magnetization in FC curve. However, the nature of this magnetic transition needs to be confirmed by neutron diffraction study in future work. The ZFC and FC curves around T_C are completely reversible as observed usually in the second-order magnetic transition. However, a large discrepancy between ZFC and FC curves appears below T_C, which is often observed in spin-glass systems,[20] narrow domain wall systems,[21,22] and materials with competing interactions.[23,24] The neutron diffraction studies have revealed that *R*FeSi (*R* = Nd, Tb, and Dy) compounds exhibit a collinear ferromagnetic structure with magnetic moments aligned along the easy *c*-axis, suggesting the high magnetocrystalline anisotropy.[17] The high anisotropy and low ordering temperature would result in the formation of narrow domain walls, which then lead to the domain wall pinning effect.[25] Therefore, this large thermomagnetic irreversibility in HoFeSi may mainly result from the domain wall pinning effect. In the ZFC mode, the magnetization is relatively small especially at low temperatures since the domain walls are pinned. However, in FC mode, the applied magnetic field during cooling prevents the pinning effect, and thus leading

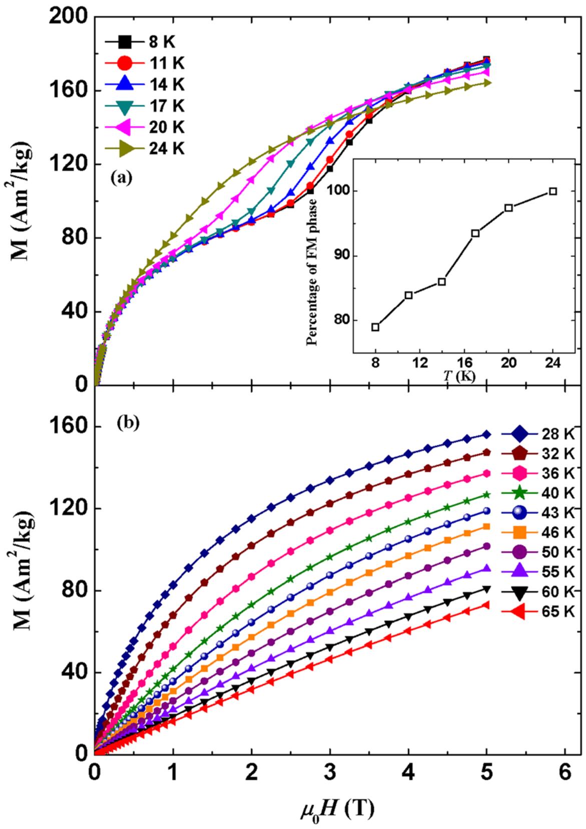

FIG. 3. (a) Magnetization isotherms of HoFeSi compound in the temperature range of 8–24 K. The inset shows the fraction of FM phase as a function of temperature estimated from magnetization isotherms. (a) Magnetization isotherms of HoFeSi compound in the temperature range of 28–65 K.

to a high magnetization in comparison with that in ZFC mode. Similar phenomenon has also been observed in ErFeSi compound.[18] In addition, considering that HoFeSi does not exhibit a completely FM state at low temperatures, the thermomagnetic irreversibility may also partly be related to the competing FM and AFM/FIM interactions.

In order to further understand the successive magnetic transitions in HoFeSi, the temperature dependences of magnetization in various magnetic fields are presented in Fig. 2(b). With the increase in magnetic field, the magnetic transition around T_C becomes sluggish and the T_C shifts to high temperature (e.g., $T_C = 34$ K at 3 T), corresponding to the typical behavior of PM-FM transition.[26] On the contrary, the T_t is driven to low temperature with increasing magnetic field (e.g., $T_t = 11$ K at 3 T), and no FM-AFM/FIM transition can be observed when the field reaches 5 T. This fact suggests the occurrence of a field-induced metamagnetic transition from AFM/FIM to FM states below T_t with increasing magnetic field.

The inset of Fig. 2(a) shows the temperature dependence of the inverse dc susceptibilities (χ^{-1}) under 1 T and the Curie-Weiss fit to the experimental data for HoFeSi compound. It is noted that the inverse susceptibility above T_C obeys the Curie-Weiss law $\chi^{-1} = (T - \theta_P)/C$, where θ_P is the paramagnetic Curie temperature and C is the Curie-Weiss constant. Based on the calculation of Curie-Weiss fit, the values of θ_P and effective magnetic moment (μ_{eff}) for HoFeSi compound are obtained to be 24.8 K and 11.25 μ_B/Ho^{3+}, respectively. The μ_{eff} value is close to the theoretical magnetic moment (10.6 μ_B) of Ho^{3+} free ion, implying the absence of localized magnetic moment on Fe atoms in HoFeSi, which is in accord with previous results on *R*FeSi compounds.[17,18] The positive θ_P value indicates that ErFeSi predominantly exhibits FM interactions in the ground state. However, it is also noted that the θ_P value is lower than T_C, revealing the possible presence of AFM or FIM moments.[27]

Figure 3 shows the magnetization isotherms of HoFeSi compound under applied fields up to 5 T with different temperature steps. It can be seen from Fig. 3(a) that the magnetization below 20 K increases sharply at low fields and tends to saturate with the increase in field at first, corresponding to the typical FM behavior. With further increasing the magnetic field, a field-induced metamagnetic transition occurs at a critical field, which can be often observed in systems with AFM or FIM phase.[28,29] This result suggests the possible presence of AFM/FIM components at low temperatures in HoFeSi compound. In addition, it is noted that the critical field, determined from the maximum of d*M*/d*H* versus *H* curve, decreases with the increase in temperature and no clear metamagnetic transition is observed when temperature is higher than T_t, proving that the AFM/FIM phase transforms into FM phase with the variation of temperature. The fraction of FM components for each magnetization isotherm can be roughly estimated by extrapolating the plateau of FM state to 5 T and is shown in the inset of Fig. 3(a).[30] The percentage of FM components is about 79% at 8 K, and it reaches nearly 100% when temperature is 24 K. This result further confirms the occurrence of FM-AFM/FIM transition around T_t, consistent with the result from *M-T* curves. On the other hand, it is found from Fig. 3(b) that HoFeSi undergoes a typical FM-PM transition in the temperature range of 28–65 K. Besides, the magnetization isotherms exhibit strong curvatures at low fields at temperatures well above T_C. Similar phenomenon has also been observed in other intermetallic compounds, and it may be attributed to the presence of short-range FM correlations above T_C caused by the magnetic polarization effect.[27,28]

The Arrott plots of HoFeSi derived from *M-H* isotherms are presented in Fig. 4. According to Banerjee criterion, a magnetic transition is expected to be first-order when the Arrott curve exhibits negative slope or inflection point; otherwise it will be second-order when the slope is positive.[31] The Arrott plots of HoFeSi below T_t (Fig. 4(a)) show clearly negative slope and inflection point, proving that the field-induced metamagnetic transition is of first-order magnetic transition. However, only positive slope is observed in Arrott plots around T_C (Fig. 4(b)), which reveals the characteristic of second-order FM-PM magnetic transition.

In an isothermal process of magnetization, the ΔS_M value can be derived from *M-H* curves by using the Maxwell relation

$$\Delta S_M(T,H) = \int_0^H (\partial M/\partial T)_H dH. \quad (1)$$

In practice, the ΔS_M value usually can be calculated using the following numerical approximation:[13,32]

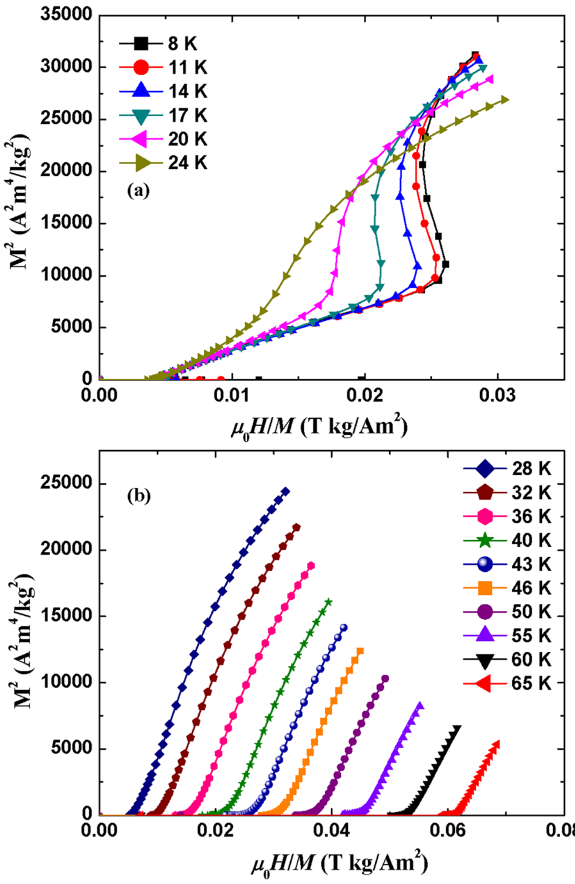

FIG. 4. (a) Arrott plots of HoFeSi compound in the temperature range of 8–24 K. (b) Arrott plots of HoFeSi compound in the temperature range of 28–65 K.

$$\Delta S_M = \sum_i \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i, \quad (2)$$

where M_i and M_{i+1} are the magnetization values measured at temperatures T_i and T_{i+1} in a magnetic field H_i, respectively. The ΔS_M of HoFeSi was estimated according to Eq. (2), and the temperature dependence of ΔS_M for different magnetic fields changes up to 5 T and is shown in Fig. 5. The HoFeSi exhibits a negative ΔS_M peak (normal MCE) around T_C, corresponding to the PM-FM transition. It is also noted that the ΔS_M peak around T_C broadens asymmetrically towards high temperatures with increasing magnetic field, which may be attributed to the presence of short-range FM correlations above T_C.[33] In contrast, the sign of ΔS_M changes gradually with the decrease in temperature and then a positive ΔS_M peak (inverse MCE) is observed around T_t due to the presence of AFM/FIM state at low temperatures. Meanwhile, the positive ΔS_M peak expands to lower temperature region with increasing magnetic field, which is attributed to the field-induced metamagnetic transition.[34] The maximum values of ΔS_M for a magnetic field change of 5 T are 6.0 and 16.2 J/kg K around T_t and T_C, respectively. Particularly, for a relatively low field change of 2 T, ΔS_M peaks around T_t and T_C reach as high as 5.6 and 7.1 J/kg K, respectively. This large MCE under low field change is preferable to practical applications since the magnetic field of 2 T can be supplied by a permanent magnet.

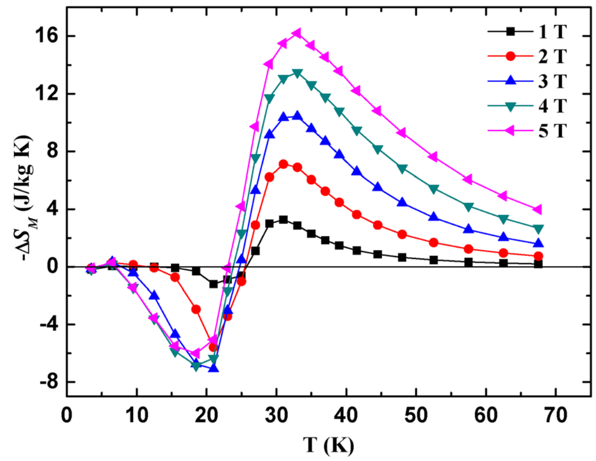

FIG. 5. Temperature dependence of magnetic entropy change ΔS_M for HoFeSi compound under different magnetic field changes up to 5 T.

This special feature of successive inverse and normal MCEs in HoFeSi compound could be utilized in some aspects, which most other materials with only normal MCE cannot satisfy. For example, (1) both inverse and normal MCEs can be utilized in one magnetic refrigerator suggested by Zhang *et al.*,[12] in which both magnetization and demagnetization processes are employed for cooling, and thus the efficiency of refrigeration may be improved greatly; (2) since the sign of ΔS_M changes at a critical temperature ($\sim$24 K), one can stabilize the temperature of a magnetic refrigerator to 24 K due to the different sign of ΔS_M around the critical point.[14]

IV. CONCLUSIONS

In conclusion, single-phase HoFeSi compound with tetragonal CeFeSi-type structure was prepared, and the magnetic properties and MCE were investigated by magnetic measurements. With the decrease in temperature, HoFeSi undergoes a PM-FM transition at $T_C = 29$ K. Another anomaly is observed at $T_t = 20$ K, which is speculated to be FM-AFM/FIM transition. In addition, a field-induced AFM/FIM-FM metamagnetic transition is observed below T_t at a critical field with increasing magnetic field. It is interesting to note that HoFeSi shows successive inverse and normal MCEs, and the ΔS_M peaks around T_t and T_C are 5.6 and 7.1 J/kg K for a relatively low field change of 2 T, respectively. This feature of successive inverse and normal MCEs could be utilized in some refrigerators with special designs and functions.

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