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Hydrostatic pressure effect on magnetic phase transition and magnetocaloric effect of metamagnetic TmZn compound

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The magnetocaloric effect (MCE) is an intrinsic thermal response of all magnetic solids which has a direct and strong correlation with the corresponding magnetic phase transition. It has been well recognized that the magnetic phase transition can be tuned by adjusting applied pressure. Therefore, we perform the high hydrostatic pressure magnetization measurements (up to 1.4 GPa) on a recently reported giant MCE material of TmZn. The results indicate that the Curie temperature of T_C increases from 8.4 K at the ambient pressure to 11.5 K under the pressure of 1.4 GPa. The field-induced first order metamagnetic transition is getting weak with increasing pressure, which results in a reduction of MCE. The hydrostatic pressure effect on the magnetic phase transition and MCE in the metamagnetic TmZn is discussed.

In recent years, the magnetocaloric effect (MCE) in magnetic materials has been well investigated, not only due to their potential applications for active magnetic refrigeration but also enable to understand the related fundamental properties of these materials^{1–8}. MCE is an intrinsic thermal response of all magnetic solids which manifests as the isothermal magnetic entropy change (ΔS_M) and the adiabatic temperature change (ΔT_{ad}) when the magnetic field is applied or removed. Magnetic refrigeration technology based on MCE is an alternative technology over the commercial gas compression/expansion refrigeration because of its promising advantages (high energy efficiency, environmental conservation, small noise, *etc.*)^{1–4}.

The MCE is the essential result of the magnetic entropy change due to the coupling of a magnetic spin system with magnetic field, and it is significant around the magnetic phase transition. Despite it has been well recognized that the magnetic phase transitions can be tuned by pressure^{9–11}, only a few works are related to the hydrostatic pressure effect on MCE^{12–17}. Morellon *et al.*¹² found that the external pressure can tune the magnetic phase transition and induce a giant MCE in $Tb_5Si_2Ge_2$, whereas the MCE in $Gd_5Ge_2Si_2$ decreases evidently with increasing pressure¹³. The peak position of the magnetic entropy change ΔS_M for $La_{0.69}Ca_{0.31}MnO_3$ shifts to higher temperatures gradually, while the maximum value of $-\Delta S_M$ is almost unchanged with increasing pressure¹⁴. As a matter of fact, a weak pressure dependence on MCE has also been reported in some MCE materials, such as, $GdCo_2B_2$ ¹⁵ and $GdCr_2Si_2$ ¹⁶ compounds. Very recently, a giant reversible MCE in metamagnetic TmZn compound was reported¹⁸. To further understand the magnetic phase transition and its correlation with MCE, in this paper, we have further performed the high hydrostatic pressure magnetization measurements on TmZn.

Results and Discussion

Figure 1 shows the temperature dependence of the zero field cooled (ZFC) and field cooled (FC) magnetization (M) measured in a magnetic field (H) of 0.1 T for TmZn under various hydrostatic pressures. All the ZFC and FC $M(T)$ curves show a paramagnetic to ferromagnetic (PM-FM) transition. The values of the Curie temperature T_C (defined as the minimum of dM/dT vs. T) are determined to be 8.4, 9.1 and 11.2 K under the pressures of 0, 0.60 and 1.40 GPa, respectively. The value of T_C in zero pressure is well consistent with previous reported results^{18,19}. The magnetic properties of TmZn have been extensively investigated thirty years ago by the specific heat, resistivity, magnetization and neutron diffraction measurements^{18–22}. The results indicated that

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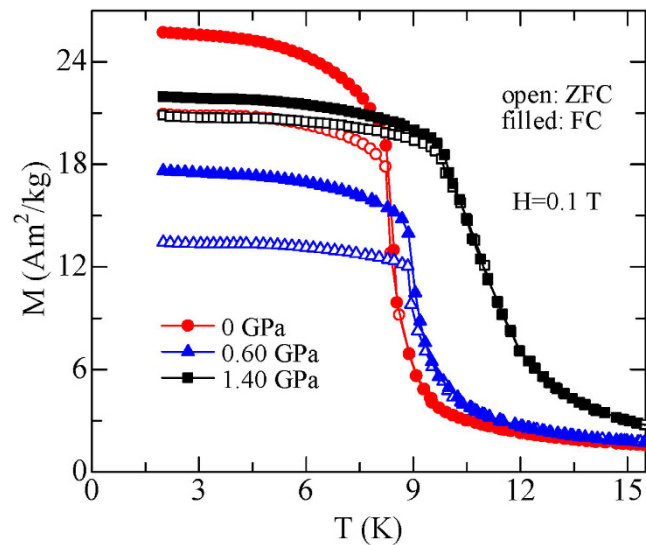


Figure 1. Temperature dependence of the zero field cooled (ZFC) and field cooled (FC) magnetization (M) under a magnetic field of 0.1 T for TmZn under the pressures of 0, 0.60 and 1.40 GPa.

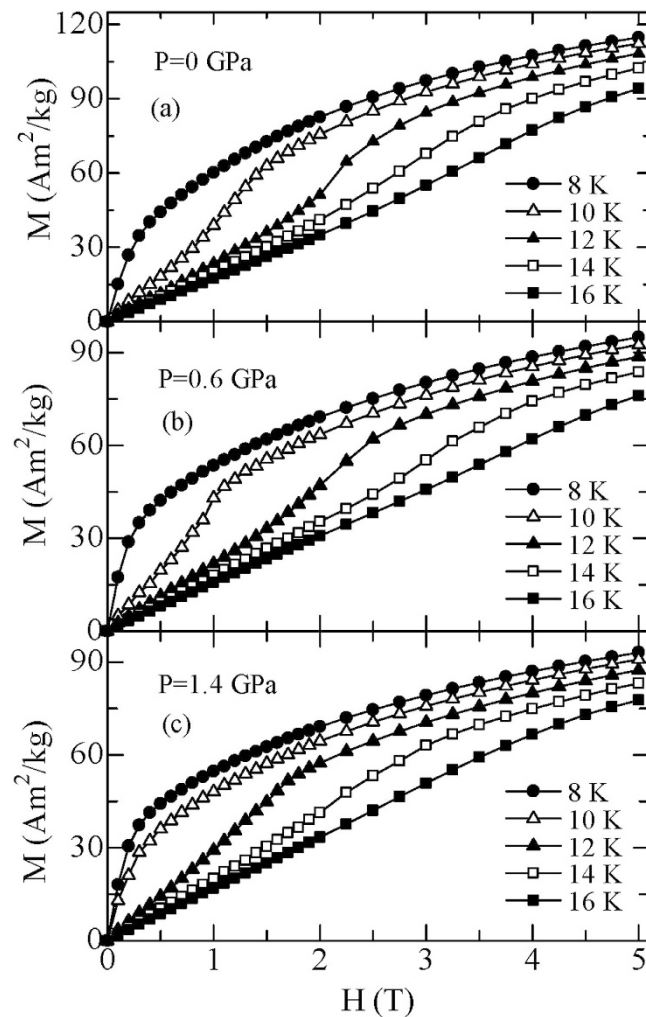


Figure 2. Magnetic field dependence of the magnetization $M(H)$ curves for TmZn at some selected temperatures under the pressures of (a) 0, (b) 0.60 and (c) 1.40 GPa, respectively.

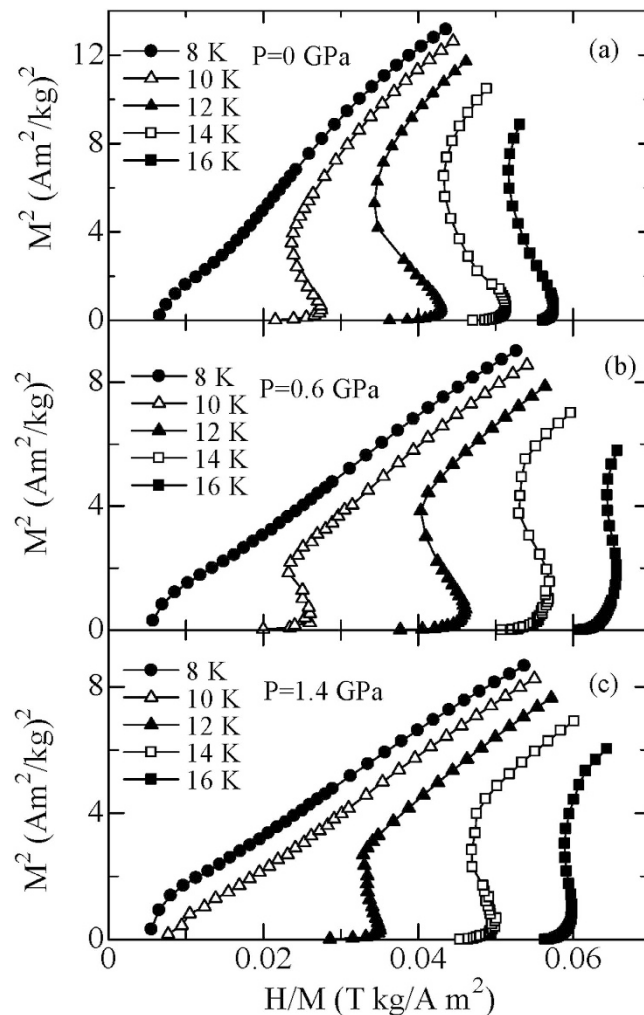


Figure 3. The Arrott plots (H/M versus M^2) for TmZn at some selected temperatures under the pressures of (a) 0, (b) 0.60 and (c) 1.40 GPa, respectively.

the strong field and temperature dependence of magnetic moment in TmZn cannot be described by a simple Rdderman-Kittel-Kasuya-Yosida (RKKY) model, and the low temperature ferromagnetic state in TmZn is probably due to the soft longitudinal spin fluctuations²³, since the low temperature magnetization is not saturate even under fields approaching 10 T¹⁸.

To investigate the pressure effect on MCE in TmZn, a set of magnetic isothermal $M(H)$ curves under the hydrostatic pressures of 0, 0.60 and 1.40 GPa with increasing and decreasing magnetic field up to 5 T for TmZn are measured. No obvious hysteresis can be observed under all the pressures for the whole temperature range. To ensure the readability of the figure, only several selected isotherms with increasing field for TmZn under 0, 0.60 and 1.40 GPa are presented in Fig. 2 for a comparison, and the corresponding Arrott plot (H/M versus M^2) curves are given in Fig. 3. Except some differences in values, the magnetic isotherms and the Arrott plots show a similar behavior under all the present pressures. I. e., a field-induced metamagnetic transition appears in a certain temperature range (around and above T_C), and the critical field shifts to higher magnetic fields with increasing temperature. Based on the Banerjee criterion²⁴, the magnetic transition is first order if some of the H/M versus M^2 curves show negative slope at some points. Therefore, the present TmZn under all the present pressures reveal a typical field-induced first order metamagnetic transition, since a clear S-shape can be observed in the Arrott plots under all the pressures (as given in Fig. 3). In details, the magnetization jump during the metamagnetic transition and the temperature range of the metamagnetic transition is getting smaller with increasing pressure. Additionally, the slop of the Arrott plot related to the strength of first order transition is getting weak with increasing pressure. These behaviors indicate that the first order metamagnetic transition of TmZn is suppressed gradually with increasing hydrostatic pressure but not breakdown up to 1.40 GPa.

Figure 4 presents the magnetic entropy change ΔS_M for TmZn under various pressures which is calculated by integrating the Maxwell's relation, $\Delta S_M(T, \Delta H) = \int_0^{\Delta H} (\partial M(H, T)/\partial T)_H dH$, using the data of magnetization isotherms $M(H, T)$. As expected, $-\Delta S_M$ exhibits a pronounced peak around T_C where the magnetization changes rapidly with varying temperature; and the peak position of $-\Delta S_M$ shifts to higher temperatures gradually which is a consequence of pressure induced T_C shifts. The values of maximum magnetic entropy change ($-\Delta S_M^{\max}$) for

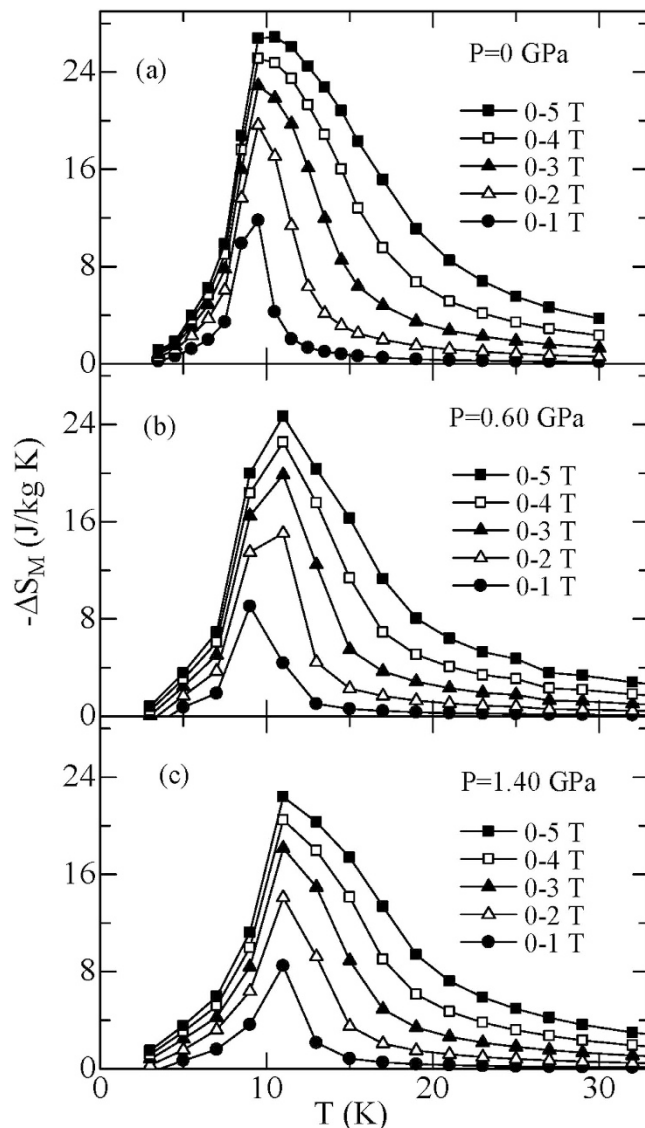


Figure 4. Temperature dependence of magnetic entropy change $-\Delta S_M$ for TmZn under the pressures of (a) 0, (b) 0.60 and (c) 1.40 GPa, respectively.

TmZn under the pressures of 0, 0.60 and 1.40 GPa are evaluated to be 11.8, 9.1 and 8.5 J/kg K for the field change of 0–1 T, to be 19.6, 15.1 and 14.1 J/kg K for the field change of 0–2 T, and to be 26.9, 24.7 and 22.4 J/kg K for the field change of 0–5 T, respectively. I. e., the MCE decreases gradually with increasing pressure. Apparently, the temperature dependence of $-\Delta S_M$ for TmZn is getting flatter and more symmetrical with increasing pressure, this is another signal of the first order magnetic phase transition is getting weak with increasing hydrostatic pressure. It is well known that the MCE has a direct and strong correlation with the corresponding magnetic phase transition. Therefore, the reduction MCE in present TmZn is related to the suppression of the first order metamagnetic transition by the applied hydrostatic pressure. Another important parameter for MCE materials is the refrigerant capacity (RC) which can be evaluated by numerically integrating the area under the $-\Delta S_M(T)$ curve at half maximum of the peak taken as the integration limits, $RC = \int_{T_1}^{T_2} |\Delta S_M| dT$, where T_1 and T_2 are the temperatures of the cold end and the hot end of an ideal thermodynamic cycle, respectively⁴. For the field change of 0–5 T, the values of RC for TmZn are 214, 203 and 141 J/kg under the pressures of 0, 0.60 and 1.40 GPa, respectively.

Conclusions

In summary, the magnetic phase transition and magnetocaloric effect in metamagnetic TmZn have been systematically investigated by magnetization measurements under high hydrostatic pressure up to 1.4 GPa. The Curie temperatures of T_C are determined to be 8.4, 9.1 and 11.2 K under the pressures of 0, 0.60 and 1.40 GPa, respectively. The field-induced first order metamagnetic transition in TmZn is suppressed gradually with increasing hydrostatic pressure but not breakdown up to 1.40 GPa. The MCE in TmZn decreases gradually with increasing

pressure. For a magnetic field change of 0–5 T, the maximum values of the magnetic entropy change of TmZn are determined to be 26.9, 24.7 and 22.2 J/kg K under the pressures of 0, 0.60 and 1.40 GPa, respectively. The corresponding values of RC are evaluated to be 214, 203 and 141 J/kg.

Methods

The polycrystalline sample of TmZn was prepared by induction melting of the high purity Tm and Zn elements in a sealed Ta-tube. Firstly, high purity Tm and Zn with stoichiometric amounts were weighted and arc-welded in a Ta-tube under an argon pressure of ca. 75 kPa. Then the Ta-tube was placed in a water-cooled sample chamber of an induction furnace and heated up to 1250 K for five minutes, following by two hours annealing at 950 K. The sample was proved to be single phase by X-ray powder diffraction and Energy Dispersive X-ray Spectroscopy. The magnetization measurements under various hydrostatic pressures with DC magnetic fields up to 5 T were performed with a commercial superconducting quantum interference device (SQUID) magnetometer by Quantum Design (MPMS-5S) from 2 to 32 K. The sample was compressed in a homemade micro-CuBe pressure cell which was filled with the mixture of Florinerts 70 and 77 as the pressure transmitting medium. The hydrostatic pressure inside the cell was determined by the superconducting transition temperature of Sn.

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Author Contributions

L.L. designed the study and prepared the sample. G.H. performed the magnetization measurements under pressures. Y.Q. and I.U. provided suggestions for the data analyses and the manuscript. L.L. prepared the manuscript and all authors reviewed it.

Additional Information

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