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Comment on "Giant anisotropy of magnetocaloric effect in $TbMnO_3$ single crystals"

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Materials showing anisotropic magnetocaloric effects could open the way for new designs of magnetic cooling. In the paper by Jin *et al.* [Phys. Rev. B **83**, 184431 (2011)], a rotating magnetocaloric effect was pointed out in $TbMnO_3$ single crystals. The reported effect arises from the rotation of $TbMnO_3$ crystals between their b and a axes. However, in this Comment we demonstrate that $TbMnO_3$ crystals generate a rotating magnetocaloric effect that is at least two times larger than that reported by Jin *et al.* On the other hand, the newly reported rotating magnetocaloric effect is not directly resulted from the magnetocrystalline anisotropy, also being in contrast with Jin *et al.* data.

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Nowadays, the search for efficient and clean cooling technologies have generated a huge interest for magnetocaloric materials that are considered as potential substitutes for the harmful fluorinated gases usually utilized by conventional refrigerators [1,2]. By using solid-state refrigerants, magnetic cooling would enable one to fully suppress the synthetic refrigerants while offering better thermodynamic efficiency [1,2]. In this context, a wide variety of magnetocaloric materials has been suggested for low- and room-temperature applications including both oxides and intermetallics [2–4]. Particularly, the RMnO$_3$ (R = magnetic rare earth) manganites have been shown to largely satisfy the requirements of low-temperature magnetic cooling [3]. In addition to their excellent magnetocaloric properties over the temperature range around 10 K, RMnO$_3$ oxides unveil better chemical and mechanical stabilities when compared with other materials such as the intermetallics [4,5]. Besides, some of the RMnO$_3$ crystals [3] show a large rotating magnetocaloric effect (RMCE) that can be obtained by spinning them in constant magnetic fields opening the way for the design of more compact and simplified magnetic cooling devices [6,7]. In order to learn more about the magnetocaloric properties of RMnO$_3$ oxides, we refer the interested reader to the review paper by Balli *et al.* [3].

Recently, the magnetocaloric properties of $TbMnO_3$ crystals have been carried out by Jin *et al.* [8]. Under the magnetic field variation of 0–7 T applied along the easy axis a, the $TbMnO_3$ crystal shows a maximum entropy change ($-\Delta S_{\max}$) of about 18 J/kg K. In a similar magnetic field change, the corresponding refrigerant capacity (RC) was found to be 390.7 J/kg. Additionally, the rotation of $TbMnO_3$ crystals between the a and b axes by an angle of 90° in a constant magnetic field of 7 T enables a maximum entropy change ($-\Delta S_{R,ba}$) of about 8.2 J/kg K to be generated, being much lower when compared with the entropy change resulting from the magnetization of $TbMnO_3$ crystals along the a axis. The corresponding adiabatic temperature change ($\Delta T_{ad,ba}$) and refrigerant capacity (RC$_{R,ba}$) reach only 6 K (5 T) and about 300 J/kg (7 T), respectively [8]. However, as shown hereafter, the $TbMnO_3$ single crystals enable one to deliver a rotating magnetocaloric effect that is at least two times larger than that reported in the work by Jin *et al.* [8], provided they are rotated in the ac plane.

The crystals investigated here were grown by using the floating zone technique [9]. The analysis of Raman signatures (not shown here) confirms that $TbMnO_3$ single crystals crystallize in a high-quality orthorhombic structure with a *Pbmn* space group. The magnetization measurements were carried out by using a superconducting quantum interference device magnetometer from Quantum Design, model MPMS XL. Magnetic isotherms [Fig. 1(a)] at low temperatures (2 K) unveil a marked anisotropic behavior where the easy, intermediate, and hard axes are aligned along the a, b, and c directions, respectively. According to thermomagnetic curves, the ordering temperature of Tb^{3+} magnetic moments was found to take place at around 9 K, in perfect agreement with that reported by Jin *et al.* [8]. On the other hand, the $TbMnO_3$ magnetization tends to saturate after overpassing a critical magnetic field of 1.4 T applied along the easy axis and reaches a maximum value of 152.4 A m^2/kg under a magnetic field of 7 T. Once again, this value is quite similar to the maximum magnetization reported in Ref. [8].

It is worth noting that the competition between different types of magnetic interactions in RMnO$_3$ manganites leads to strongly frustrated systems [10]. This is usually associated with different magnetic and electric transitions involving Mn^{3+} and R^{3+} ions [3,10–14]. Regarding $TbMnO_3$ crystals, in addition to the ordering of Tb^{3+} magnetic moments close to 9 K, other phase transitions involving the Mn^{3+} sublattice that correspond to the onset [3,11–14] of incommensurate antiferromagnetic and spiral magnetic orders occur around $T_N = 42$ K and $T_L = 27$ K, respectively. The latter transition induces a spontaneous electric polarization along the hard axis c [11]. However, because it is extremely challenging to orient the magnetic moments of Mn^{3+} ions parallel to the magnetic field direction in RMnO$_3$ manganites [3], the MCE is usually investigated in the temperature range around the ordering point of R^{3+} moments. So, as in Jin *et al.* [8], the entropy

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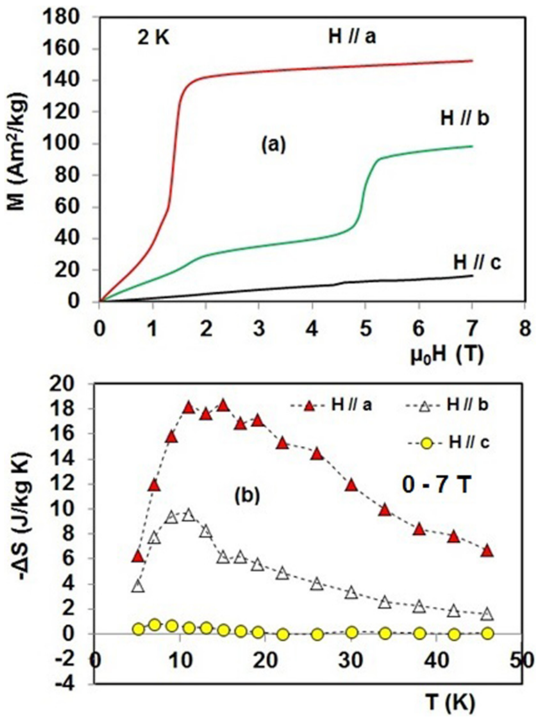

FIG. 1. (a) Isothermal magnetization curves at 2 K of the $TbMnO_3$ single crystal along its crystallographic axes. (b) Its isothermal entropy variation as a function of temperature for a field changing from 0 to 7 T along the *a*, *b*, and *c* axes.

change (ΔS) resulting from the magnetization of $TbMnO_3$ was recalculated by integrating the well-known Maxwell relation [2–4] over the temperature range around 10 K. It is worth noting that the utilization of the Maxwell relation to determine the entropy change was a subject of controversy [4,15–17]. However, this mainly concerns magnetocaloric materials exhibiting large hysteretic effects resulting in a phase-separated state (out of equilibrium) [15], which is not the case of $TbMnO_3$ single crystals since they show a negligible hysteresis (not shown here). In addition, Midya *et al.* [18] have recently demonstrated that the Maxwell relation is also a very good tool to evaluate the MCE in multiferroics. They found that the deduced entropy change from magnetization measurements of $EuTiO_3$ is in perfect agreement with that obtained from specific heat data [18].

The isothermal entropy change as a function of temperature and magnetic field is reported in Fig. 1(b) for the three crystallographic axes of $TbMnO_3$. Along the easy axis *a*, $-\Delta S$ reaches a maximum value of about 18 J/kg K for a magnetic field changing from 0 to 7 T, being equal to that reported in Jin *et al.* [8]. Moreover, as shown in Fig. 1(b), the isothermal entropy change reveals a gigantic anisotropy between the *a* and *c* axes. In the field change of 7 T, the obtained $-\Delta S$ along the easy axis *a* at 11 K is about 32 times larger than its equivalent along the hard axis *c*. In contrast, the ΔS anisotropy is less pronounced between the *a* and *b* axes. According to Ref. [8], the isothermal entropy change along the *a* axis exceeds that along the *b* axis only by a factor of 2 in the field change of 7 T, which is also confirmed by our reported data in Fig. 1(b). This low anisotropy of ΔS would explain the relatively moderate value of RMCE reported by Jin *et al.* for the $TbMnO_3$ single crystal [8]. In fact, the authors [8] have considered the *b* axis as the hard orientation of the single crystal which is incorrect. According to Fig. 1(a), the hard axis is clearly parallel to the c direction, whereas the b axis rather corresponds to the intermediate orientation.

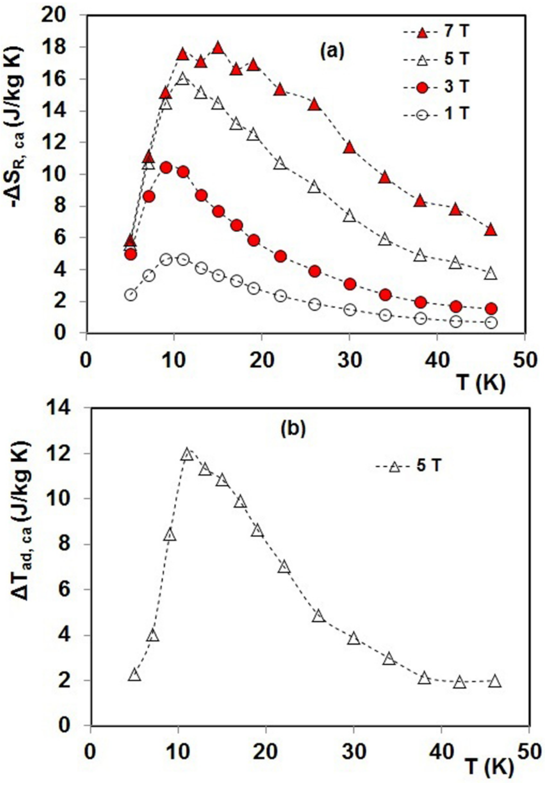

FIG. 2. (a) Isothermal entropy change resulting from the rotation of $TbMnO_3$ single crystal around the *b* axis in several constant magnetic fields, initially parallel to the *c* axis. (b) Associated adiabatic temperature change under a constant magneic field of 5 T.

The isothermal entropy change arising from the rotation of $TbMnO_3$ single crystals within the *ac* plane was also determined from magnetization measurements. Considering initially the magnetic field parallel to the *c* axis, the rotation of the $TbMnO_3$ single crystal around its intermediate axis by an angle of 90° leads to a change in the full entropy by [3–8]

$$\Delta S_{R,ca} = \Delta S(H \parallel a) - \Delta S(H \parallel c), \tag{1}$$

where ΔS $(H \| a)$ and ΔS $(H \| c)$ are the entropy changes resulting from the application of magnetic field along the easy and hard directions, respectively. The temperature dependence of $\Delta S_{R,ca}$ under some representative magnetic fields is plotted in Fig. 2(a). For a constant magnetic field of 7 T applied within the *ac* plane, the rotation of $TbMnO_3$ around its *b* axis results in a maximum $-\Delta S_{R,ca}$ of about 18 J/kg K, which is more than two times larger if compared with that ($-\Delta S_{R,ba}$) reported in Ref. [8]. More interestingly, $-\Delta S_{R,ca}$ does not show any tendency to decrease when increasing magnetic field up to 7 T. This contrasts to the entropy change within the *ab* plane reported in Jin *et al.* [8]. According to Ref. [8], $-\Delta S_{R,ba}$

begins to saturate after overpassing a magnetic field of about 3.5 T and significantly decreases for magnetic fields higher than 5 T. This can be mainly explained by the switch of Mn^{3+} magnetic structure from the *bc* plane to the *ab* plane via a metamagneticlike transition [Fig. 1(a)]. The latter is induced by magnetic fields of roughly 4.8 T when applied along the *b* axis [3,8,11–14]. Indeed, at temperatures below $T_L = 27$ K, the Mn^{3+} magnetic moments order in a commensurate phase by forming a spiral magnetic structure in the *bc* plane with the propagation vector along the *b* direction [12–14]. Due to the strong interplay between the Tb and Mn moments, the magnetic modulation of Mn^{3+} moments can be reoriented under relatively low magnetic fields giving rise to a sharp metamagnetic transition along the *b* axis. Consequently, the magnetic anisotropy is largely reduced in the *ab* plane, leading to relatively moderate values of $-\Delta S_{R,ba}$ [8].

In addition to ΔS, the adiabatic temperature change $\Delta T_{ad,ca}$ associated with the RMCE in the *ac* plane was also investigated. This thermodynamic quantity is an important practical parameter that determines the magnitude of temperature spans in magnetic cooling devices. Therefore, as in Jin *et al.* [8], the $\Delta T_{ad,ca}$ can be approached by

$$\Delta T_{ad,ca} = -\frac{T}{C_P}\Delta S_{R,ca}, \tag{2}$$

where the specific heat (C_P) values were taken from Ref. [11]. The temperature dependence of $\Delta T_{ad,ca}$ evaluated for a constant magnetic field of 5 T is plotted in Fig. 2(b). As shown, the $\Delta T_{ad,ca}$ resulting from the rotation of $\mathrm{TbMnO_3}$ single crystals in the *ac* plane attains a maximum value of approximately 12 K, being about two times larger than that obtained within the *ab* plane [8].

The RC is another important magnetocaloric parameter because it takes into account both the MCE magnitude and the magnetocaloric working temperature range of materials [2,3]. The $\mathrm{RC}_{R,ca}$ associated with the rotation of $\mathrm{TbMnO_3}$ crystals in the *ac* plane was found to be as large as 405 J/kg for 7 T, and instead only about 300 J/kg for the ab plane [8].

The last point in this Comment concerns whether the magnetocrystalline anisotropy is fully responsible for the RMCE in $\mathrm{TbMnO_3}$ crystals, as claimed in Ref. [8]. The best way to check this is to utilize the coherent rotational (CR) model [8,19] that enables us to evaluate the entropy change resulting from the magnetocrystalline anisotropy, namely, ΔS_{MCA}. In Fig. 3, we report the angle β dependence of ΔS_{MCA} (ΔS_R) within the *ab* and *ac* planes under constant magnetic fields, initially parallel to the *b* and *c* axes, respectively. β represents the angle between the magnetic field direction and the easy axis.

It is worth noting that Jin *et al.* [8] have also studied the RMCE origin in $\mathrm{TbMnO_3}$ crystals by using the CR model at 15 K. Accordingly, they claimed that the resulting RMCE within the *ab* plane originates directly from the magnetocrystalline anisotropy. Their findings are confirmed by the reported data in Fig. 3(a), since our calculated $\Delta S_{\mathrm{MCA},ba}$ is in fair agreement with their experimental measurements [8]. However, as in Ref. [8], the application of the CR model to the *ab* plane was only performed for temperatures relatively far above (15 K) the ordering point of Tb^{3+} magnetic moments. In this temperature range, the magnetization along the *b* axis evolves linearly with magnetic field making easier the determination of anisotropy constants by minimizing the crystal energy [8,19]. In contrast, the magnetization below 9 K unveils a marked jump under magnetic fields higher than 4 T [Fig. 1(a)] that is caused by the reorientation of Mn^{3+} magnetic moments [10–14]. This means that in addition to the magnetocrystalline anisotropy induced by the $4f$ spin-orbital coupling, the strong interplay between the magnetic moments of Tb^{3+} and Mn^{3+} sublattices [10,14] which is responsible for the metamagnetic transition must also be taken into account. The latter point is ignored in CR model-based calculations. It is then not evident to conclude that the MCE arising from the rotation of $\mathrm{TbMnO_3}$ crystals between the *a* and *b* axes is directly contributed from the magnetocrystalline anisotropy as inferred by Jin *et al.* [8]. By using the Clausius-Clapeyron equation given by [3]

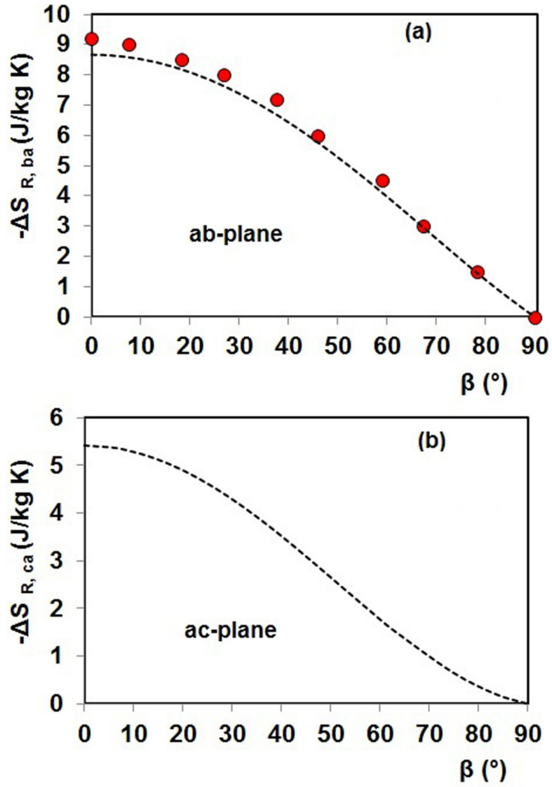

FIG. 3. (a) Calculated entropy change (dashed line) corresponding to the rotation of $\mathrm{TbMnO_3}$ between the *a* and *b* axes in a constant magnetic field of 5 T, initially parallel to the *b* axis at 15 K. Circles represent experimental data taken from Ref. [8]. (b) Calculated entropy change corresponding to the rotation of $\mathrm{TbMnO_3}$ between the *a* and *c* axes in a constant magnetic field of 7 T, initially parallel to the *c* axis at 11 K.

$$\Delta S = -\Delta M\frac{dB_C}{dT} = -\Delta M\left(\frac{dT_T}{dB}\right)^{-1}, \tag{3}$$

where B_C is the critical field and ΔM is the magnetization jump, we found that the MCE along the *b* axis at temperatures closer to 2 K originates mainly from the metamagnetic transition. For example, at 3 K, the application of a magnetic field of 5.2 T following the *b* axis generates a negative MCE

[20] of $\Delta S = 7\,\mathrm{J/kg\,K}$, where the metamagnetic region contributes for about 6 J/kg K. On the other hand, the calculated $-\Delta S_{\mathrm{MCA},ca}$ [Fig. 3(b)] reaches a maximum value of only 5.42 J/kg K (under 7 T) when the $\mathrm{TbMnO_3}$ single crystal is rotated by an angle of 90° around its intermediate axis at 11 K, being much lower than the experimental value (18 J/kg K under 7 T) reported in Fig. 2(a). This clearly underlines the fact that the RMCE within the *ac* plane is also not directly arising from the magnetocrystalline anisotropy. In this plane, additional factors could contribute to the RMCE such as thermal fluctuations and spin-flop processes involving the Mn sublattice [21,22]. This result also points out the complexity of $\mathrm{TbMnO_3}$ magnetocrystalline anisotropy on account of its complex magnetic structure [3,10–14]. In fact, the model of magnetocrystalline anisotropy and Zeeman energy reported in the paper by Jin *et al.* [8] is not completely suitable to describe the Tb subsystem in $\mathrm{TbMnO_3}$. At low temperatures, $\mathrm{Tb^{3+}}$ ions in manganites should be considered as Ising ions since their ground state in a crystal field is quasidoublet with a strong anisotropy of g factor with main components in the *ab* plane. Thereby, the magnetization at saturated states along the a and b axes must be different. In addition, there is an exchange interaction of Tb and Mn subsystems, leading to a complicated physical picture.

To sum up, we have revised the reported rotating magnetocaloric effect in $\mathrm{TbMnO_3}$ single crystals. Our findings unveil that the RMCE shown by $\mathrm{TbMnO_3}$ is much larger than that previously reported in Jin *et al.* [8]. This is because in Ref. [8], the $\mathrm{TbMnO_3}$ single crystal is rotated between the easy axis a and the b axis that was assumed by the author as the hard direction. In fact, the b orientation corresponds to the intermediate axis, while the hard direction is rather along the c axis. When rotating the $\mathrm{TbMnO_3}$ single crystal in the *ac* plane, the resulting RMCE in terms of both isothermal entropy and adiabatic temperature changes is at least two times larger than that reported in Ref. [8]. In addition, the application of a coherent rotational model to $\mathrm{TbMnO_3}$ crystals reveals that there is no clear evidence regarding the fact that the RMCE is directly resulted from the magnetocrystalline anisotropy, and the latter is more complex than previously expected.

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