Magnetodielectric and magnetoelastic properties of spinel Mn$_3$O$_4$

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Abstract. The magnetodielectric and magnetoelastic properties of spinel Mn$_3$O$_4$ with the orbital degree of freedom in the eg state of the Mn$^{3+}$ site were investigated. We found that strain ($\Delta L/L$) shows anomalies at the magnetic phase transition temperatures and is anisotropic against the crystallographic axis. We also found that this compound exhibits large magnetic field ($H$) dependences of $\Delta L/L$, details of which are different at three different magnetic phases. Similar anomalies and $H$ dependence are observed in dielectric measurements. These behaviors can be explained by the inverse effect of single-ion spin anisotropy.

Spinel Mn$_3$O$_4$ has Mn$^{2+}$ ions ($3d^5$) at the tetrahedral site of the spinel structure without the orbital degree of freedom and Mn$^{3+}$ ions ($3d^4$) at the octahedral site with the orbital degree of freedom. According to the previous reports [1], this compound has a tetragonally distorted structure ($a < c$) below the structural phase transition temperature, $T_s = 1443$ K, which can be explained by the Jahn-Teller distortion at the Mn$^{3+}$ site. Regarding magnetism, this compound exhibits successive magnetic phase transitions at $T_N = 43$ K, $T_1 = 39$ K, and $T_2 = 33$ K [2, 3]. For $T_1 < T < T_N$, which is called a Yafet-Kittel phase, the Mn$^{2+}$ spins align along the [110] direction in the cubic settings and the sum of the Mn$^{3+}$ spins align to the opposite direction (i.e. the [-1-10] direction), but the each Mn$^{3+}$ spins are canted from the [-1-10] direction to the [001] or [00-1] direction. Below $T_1$, the magnetic unit cell is enlarged along the [110] direction due to the modulation of the Mn$^{3+}$ spin alignment. The magnetic structure is incommensurate with the chemical lattice for $T_2 < T < T_1$, which is called $\sqcup$ incommensurate $\sqcup$ phase. However, the magnetic structure become commensurate again below $T_2$, where the magnetic cell is coincide with the doubled chemical cell along the [110] direction.

Recently, the magnetodielectric and magnetoelastic properties of the polycrystalline Mn$_3$O$_4$ have been reported [4, 5]. This compound exhibits a large magnetic field ($H$) dependence of both dielectric constant (magnetocapacitance) and strain (magnetostriction) below $T_N$. However, since Mn$_3$O$_4$ is magnetically and crystallographically anisotropic, the studies using single crystals are needed to clarify the magnetodielectric and/or magnetoelastic properties of this compound.

Figure 1(a) shows the temperature ($T$) dependence of magnetization ($M$) along the [100], [110], and [001] direction at 100 Oe in the field cooling (FC) process. $M$ increases sharply at $T_N$ with decreasing $T$, which indicates the onset of the Yafet-Kittel ordering. Figure 1(b) shows the magnetic field ($H$) dependence of $M$ at 5 K. $M$ along the [001] is much smaller than that along the [100] and [110] direction at low [Fig. 1(a)] and high field [Fig. 1(b)]. This indicates that the
[001] direction is the magnetically hard axis. Though there exist the magnetic anisotropy in the ab plane at low field region, the anisotropy almost disappears above 1 T. This indicates that the [110] direction is an easy axis of magnetization with relatively low in-plane anisotropy. Figure 1 (a) also shows the T dependence of M along the [110] direction in the zero field cooling (ZFC) process. As can be seen, the small drops are observed at T2. These behaviors are consistent with literature [6].

Figure 2(a) shows the T dependence of strain (∆L/L) without applied H. As can be seen, the ∆L/L is anisotropic between the c axis and the ab plane, though anisotropy was hardly observed in the ab plane. The ∆L/L along the ab plane shows a steep decrease at T_N. The ∆L/L along the c axis also has an anomaly around T1. These anomalies at the magnetic transition temperatures indicate the correlation between magnetism and strain in this compound. Figure 2(b) shows the T dependence of dielectric constant (ε1) without applied H. The anisotropy and anomalies at the magnetic transition temperatures are observed, indicating the correlation between magnetism and dielectric properties in this compound. Here, it should be noted that the magnitude of the decrease of ∆L/L at T_N is ~ 2 × 10^-4, which is one order of magnitude smaller than that of ε1 (~ 10^-3). This indicate that the anomaly of ε1 is not solely owing to the lattice expansion.

Figure 3(a) shows the T dependence of ∆L/L along the [100] direction with applied H parallel and perpendicular to ∆L/L in the ab plane. As can be seen, the ∆L/L increases for ∆L || H but decreases for ∆L ⊥ H, indicating that this compound elongated parallel to the direction of H but contracted perpendicular to H in the ab plane. The magnitude of the magnetostriction reaches to ~ 0.2 % at 20 K and 5 T, which is two orders of magnitude larger than that of conventional magnetostriction (~ 10^-3). Figure 3(b) shows the magnetic field (H) dependence of the magnitude of magnetostriction [∆L(H)/L(0)] in the ab plane at 20 K. As can be seen, ∆L(H)/L(0) along the [100] direction is much larger than that along the [110] direction. As mentioned above, however, the magnetization is isotropic in the ab plane [Fig. 1 (b)] above 1 T. Thus the anisotropy of magnetostriction does not originate from the magnetic anisotropy in the ab plane.

Figure 3(c) shows the T dependence of ∆L(H)/L(0) for ∆L || H up to 1 T. ∆L(H)/L(0) sharply increases at T_N. In the Yafet-Kittel phase (T1 < T < T_N), ∆L(H)/L(0) increases with decreasing T down to T1. Once T is lowered below T1, the ∆L(H)/L(0) is suppressed...
and exhibits a flat \( T \) dependence in the incommensurate phase. However, the \( \Delta L(H)/L(0) \) increases with decreasing \( T \) again below \( T_2 \) (the cell doubled phase). It should be noted that \( \Delta L(H)/L(0) \) at 1 T is much larger than that at 0.5 T in the cell-doubled phase while there is little difference between them in the Yafet-Kittel phase. These results indicate that the magnetoelastic properties of Mn\(_3\)O\(_4\) strongly depends on the magnetic structure. It should be also noted that \( \varepsilon_1 \) exhibits similar magnetic field dependence (not shown) \([7]\).

Before discussing a possible origin of magnetostriction below \( T_N \), let us consider the magnetic structure of Mn\(_3\)O\(_4\). As mentioned above, the Mn\(^{2+}\) and Mn\(^{3+}\) spins lie on the (1-10) plane and net magnetic moment is directed to the [110] direction in the Yafet-Kittel phase \((T_1 < T < T_N)\). Since the magnetic anisotropy in the \( ab \) plane disappears above 1 T, the net magnetic moment can be rotated in the \( ab \) plane around the [001] axis with applied magnetic field \((H)\). Thus the Mn\(^{3+}\) spins are align along the direction between the [-100] and [001] (or [00-1]) with applied \( H \) along the [100] direction.

The \( e_g \) orbitals of Mn\(^{3+}\) site are split into the lower \( z^2 \) orbital and the higher \( x^2 - y^2 \) orbital due to the Jahn-Teller effect and the former orbital is occupied by a \( d \) electron. However, once the Mn\(^{3+}\) spin has the spin component parallel to the [-100] direction, the orbital oriented the [100] direction \((x^2 \) orbital or \( z^2 - x^2 \) orbital\) prefers to be occupied by an electron due to the single ion spin anisotropy. Thus the occupied \( x^2 \) \((\text{or } z^2 - x^2)\) orbital state is mixed with the occupied \( z^2 \) orbital state at the Mn\(^{3+}\), as shown in Fig. 3(d). As a result, the \( e_g \) orbital of Mn\(^{3+}\) site become anisotropic in the \( ab \) plane and the lattice is enlarged along the direction of the occupied orbital and contracted perpendicular to that direction. This is responsible for the anisotropic magnetostriction in the \( ab \) plane. However, when \( H \) is applied along the [110] direction, such in-plane orbital anisotropy does not appear, since the \( x^2 \) orbital and \( y^2 \) orbital are occupied equivalently. Thus a magnitude of magnetostriction with \( \Delta L/L \parallel [110] \) is much smaller than that along the [100].

The magnetostriction in the cell-doubled phase \((T_2 < T < T_1)\) can be explained in same manner, because the magnetic structure in that phase is coplanar one. However, according to Jensen \textit{et al.} \([2]\), the magnetic structure in the incommensurate phase is conical structure, where

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**Figure 2.** (a) Temperature \((T)\) dependence of strain \((\Delta L/L)\) along the [100] (right axis, closed circles), [110] (right axis, open circles), and [001] (left axis, closed circles) direction without applied magnetic field \((H)\). (b) \( T \) dependence of dielectric constant \((\varepsilon_1)\) along the [100] (left axis) direction without applied \( H \). The inset shows the \( T \) dependence of \( \varepsilon_1 \) along the [100] around \( T_1 \) and \( T_2 \).
the rotation axis of the Mn$^{3+}$ spins is opposite to the direction of the Mn$^{2+}$ spin. In this case, since the Mn$^{3+}$ spins are oriented to both the [100] and [010] direction, the $x^2$ and $y^2$ orbitals are equally occupied. Thus the orbital anisotropy in the $ab$ plane is not induced by the application of $H$ along the [100] direction in the incommensurate phase unlike in the coplanar spin phase (the Yafet-Kittel and cell-doubled phases).

In conclusion, we measured the dielectric constant and strain of Mn$_3$O$_4$ with applied magnetic field. We found that the dielectric constant and strain have anomalies at the magnetic phase transition temperatures, indicating the correlation between the magnetic, dielectric, and elastic properties in this compound. We also found that this compound exhibits a large magnetostriction in the magnetically ordered phase, whose behavior against the magnetic field depends on the magnetic structure. These results can be explained by the change orbital state due to the single ion spin anisotropy on the Mn$^{3+}$ site.

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