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Magnetodielectric coupling in $MnCr_2O_4$ spinel

N. Mufti, G.R. Blake, T.T.M. Palstra *

Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands

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ABSTRACT

We have investigated the magnetic and dielectric properties of polycrystalline samples of the spinel $MnCr_2O_4$. Below the ferrimagnetic ordering temperature at T_N~43 K, both magnetization and dielectric measurements show signatures of the onset of a conical structure at T_s~17 K and a lock-in temperature at T_f~14 K. These values are similar to those previously reported for single-crystal samples, where the spiral structure is short-range ordered (SRO) at low temperatures. The application of magnetic field suppresses the dielectric anomaly at T_f indicating that the coherence length of the ordering increases. $MnCr_2O_4$ exhibits a symmetrical magnetodielectric response between T_f and T_s that scales with the square of the magnetization. This suggests that the magnetodielectric coupling originates from the P^2M^2 term in the free energy expansion. The magnetodielectric response becomes asymmetric with respect to field below T_f.

1. Introduction

Multiferroics, materials in which ferromagnetism and ferroelectricity coexist, have attracted much attention in recent years. If the coupling between the magnetic and ferroelectric order (magnetodielectric coupling) is strong enough, multiferroics potentially allow the manipulation of electric and magnetic moments by magnetic and electric fields, respectively. However, there are still rather few multiferroics known and the magnetodielectric (MD) coupling in many of them is weak. This is largely due to the fact that in typical ferroelectric oxides the creation of an electric dipole moment involves charge transfer between the occupied 2p-orbitals of oxygen and the empty d-shell of the metal ions. The common mechanism of ferroelectricity thus excludes transition metals with partially filled d-orbitals and hence the coexistence of magnetic moments and ferroelectric order [1]. Nevertheless, in recent years an increasing number of multiferroics have been discovered in which ferroelectricity arises from different mechanisms. For example, ferroelectricity can be directly induced by frustrated magnetic ordering in materials such as $TbMnO_3$, $TbMn_2O_5$, and $Ni_3V_2O_8$ [1–4], which naturally leads to strong magnetodielectric coupling. One feature common to many of the frustrated magnet multiferroics is the existence of a spiral or helical spin structure. Here, the direction of the spontaneous polarization is perpendicular to both the magnetic propagation vector and to the spin plane of the spiral. Although the microscopic mechanisms involved in the magnetodielectric coupling in this class of multiferroics are being widely studied both experimentally and theoretically, in many cases the mechanisms are not fully understood, especially regarding the strength of the coupling. Therefore, it is important to investigate magnetodielectric coupling in a wide range of frustrated magnet multiferroics.

The materials MCr_2O_4 (M = Mn and Co) are ferromagnetic spinels, in which the M^{2+} cations occupy the tetrahedral (A) sites and the Cr^{3+} cations occupy the octahedral (B) sites. The onset of collinear ferrimagnetic ordering occurs at 51 and 93 K in single-crystal samples, respectively [5]. A further magnetic transition occurs at T_s~18 and 26 K, respectively, where a short-range-ordered (SRO) spiral component develops giving a conical magnetic structure. The largest coherence lengths of the spiral at low temperatures are of the order of 10 nm for $MnCr_2O_4$ and 3.5 nm for $CoCr_2O_4$, respectively. Nevertheless, whatever the correlation length of the spiral, it is thought to be the result of weak geometrical frustration on the spinel B-site; magnetic exchange interactions between the A and B sites limit but do not completely suppress the frustration. Recently, Yamasaki et al. have reported the presence of ferroelectricity in $CoCr_2O_4$ single crystals [7], making it one of the few materials to exhibit the coexistence of ferromagnetic and ferroelectric states. The onset of polarization occurs at T_s~26 K along the $(1\bar{1}0)$ direction and the polarization can be reversed by switching the direction of the applied magnetic field. This strong magnetodielectric coupling is in good agreement with the theoretical prediction of the spin current model for magnetic ferroelectricity proposed by Katsura et al. [8]. These results prompted us to investigate the magnetic and dielectric properties of $MnCr_2O_4$, which has a similar magnetic structure to that of $CoCr_2O_4$. Moreover, the nature of

* Corresponding author. Tel.: +31 50 363 4440; fax: +31 50 363 4441.
E-mail address: t.t.m.palstra@rug.nl (T.T.M. Palstra).

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the magnetodielectric coupling in these systems has been little explored.

2. Experiment

Polycrystalline $MnCr_2O_4$ was prepared by solid state reaction using a stoichiometric mixture of MnO_2 and Cr_2O_3. The mixture was pelletized by applying hydraulic pressure at 600 bar and sintered at 1300 °C in flowing argon for 24 h. X-ray powder diffraction at room temperature was performed using a Bruker D8 diffractometer with Cu-Kα radiation. Magnetization measurements were performed using a Quantum Design MPMS-7 SQUID magnetometer. The capacitance was measured using an AH-2500A capacitance bridge and a Quantum Design PPMS.

3. Results and discussion

Room-temperature powder X-ray diffraction measurements showed that the $MnCr_2O_4$ sample was single-phase; $MnCr_2O_4$ adopts the cubic spinel structure with space group $Fd\text{-}\bar{3}m$. The lattice parameter of our sample was 8.3970(9) Å, close to the previously reported value of 8.410 Å [9].

The magnetic susceptibility of $MnCr_2O_4$ at different magnetic fields is shown in Fig. 1 (a). The onset of ferrimagnetic ordering at T_N~43 K at 0.1 T is close to the value previously reported for polycrystalline samples at 45 K [9], but lower than that reported for single crystals at 51 K [5]. The value of T_N initially increases with applied magnetic field and then becomes difficult to identify, as the transition becomes broader. We also observe anomalies at

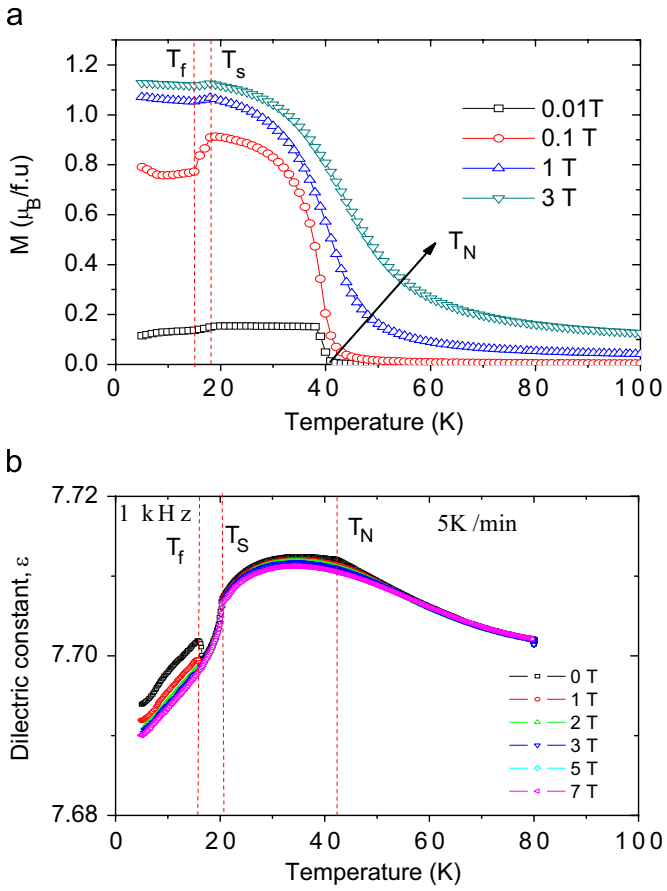

Fig. 1. Temperature dependence of (a) magnetization and (b) dielectric constant of $MnCr_2O_4$ in different applied magnetic fields.

T_s~18 K and T_f~15 K, which correspond to the temperatures where the spiral component appears and to the "lock-in" transition at which the spiral becomes fully developed, as reported by Tomiyasu et al. [5]. The behavior of our polycrystalline sample thus resembles that of single crystals, in contrast to the polycrystalline samples of $CoCr_2O_4$ studied by Lawes et al. [6], for which it was argued from specific heat data that the correlation length of the spiral state is sample dependent; in the polycrystalline samples a long-range ordered (LRO) spiral develops below T_s [6].

The temperature dependence of the dielectric constant of $MnCr_2O_4$ is shown in Fig. 1(b). Three anomalies are apparent at approximately the same temperatures as the magnetic transitions. This result is more similar to the dielectric properties of single-crystal $CoCr_2O_4$ [7] than those of polycrystalline samples, for which no dielectric anomaly was observed at T_f [6]. The small difference in transition temperatures between the magnetization and dielectric measurements is probably due to differences in temperature between the sensor and sample during heating. When a magnetic field is applied, the dielectric anomalies at T_N~43 K and T_f~15 K are both suppressed. In the case of T_N, this is most likely due to the broadening of the ferrimagnetic transition that occurs with increasing magnetic field (see Fig. 1(a)). We suggest that the suppression of the dielectric anomaly at T_f, results from an increase of the correlation length of the magnetic spiral structure. We note that in the absence of a magnetic field $MnCr_2O_4$ has two sets of SRO spiral domains with propagation vectors parallel to the [1 1 0] and −[1 1 0] directions for an easy axis parallel to [1 $\bar{1}$ 0]; the correlation length is approximately 10 nm below T_f [5]. When an external magnetic field is applied the spins will tend to align with the field, and consequently the propagation vectors in the two types of domains will also become aligned in the same direction. Therefore, we expect the correlation length of the spiral structure to increase with field, resulting in a suppression of the dielectric anomaly at T_f. This scenario is based on our dielectric and magnetic measurements, and further measurements such as neutron scattering are needed to confirm it.

Fig. 2 shows the magnetization and magnetodielectric response measured as a function of magnetic field at different temperatures below T_N. The most striking feature in the magnetization is a step-like increase at H~0.2 T; there is almost no difference in the behavior of the magnetization with field at representative temperatures below T_f (5 K), T_s (17 K), and T_N (25 K). In contrast, magnetocapacitance measurements, shown in Fig. 2(b), show unusual behavior in which the profile of the magnetocapacitance develops from an asymmetric shape at temperatures below T_f to a symmetric shape in the region between T_f and T_s. The magnetocapacitance is plotted in terms of the magnetodielectric response, defined as $MD = \varepsilon(H)-\varepsilon(0)/\varepsilon(0)$, where $\varepsilon(H)$ is the dielectric constant under field and $\varepsilon(0)$ is the dielectric constant in zero-field. Although our data are insufficient to fully explain the asymmetric magnetodielectric behavior, we suggest that the increasing correlation length of the spiral structure with increasing field below T_f might be responsible. In this scenario we assume that the magnetodielectric response on going from the SRO (low magnetic field) to LRO (high magnetic field) state is smaller than that arising in the opposite direction. Further investigation of the magnetodielectric response on single crystals might give a better understanding of this phenomenon. Similarly asymmetric behavior has previously been observed in Mn_3O_4, for which it was argued that the asymmetry is due to the magnetic hysteresis present at low temperatures [10]. We exclude this argument because we do not observe magnetic hysteresis in our magnetization measurements, as shown in the insert of Fig. 2(a).

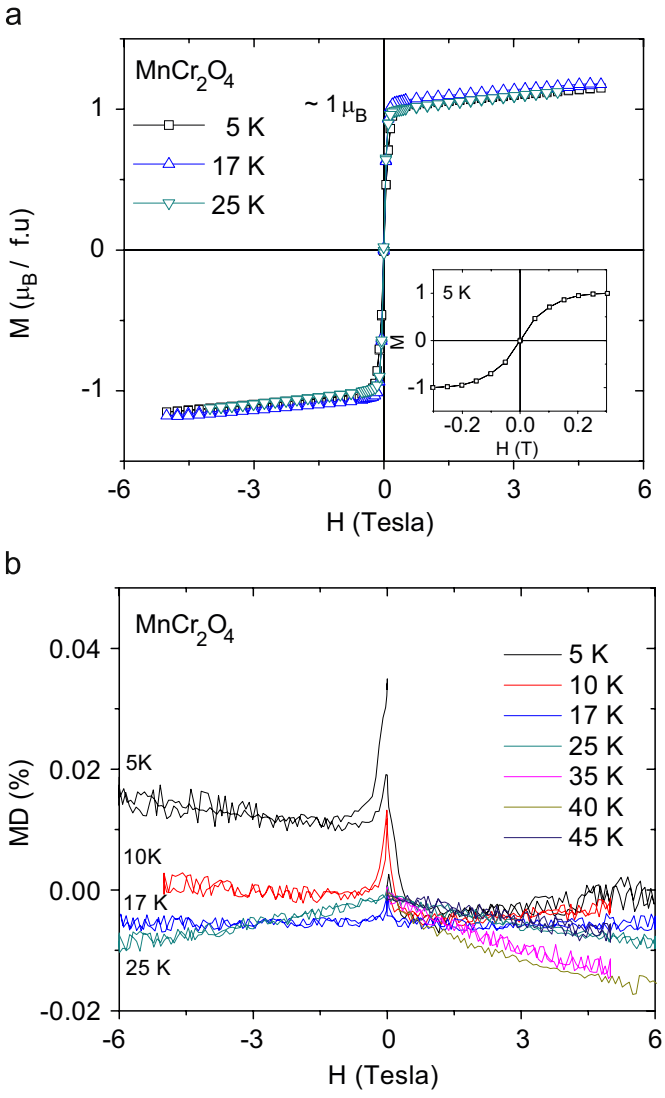

Fig. 2. Magnetic field dependence of (a) magnetization and (b) magnetodielectric response (see text for definition) of $MnCr_2O_4$ at various temperatures. The inset shows an expanded view of the magnetization at 5 K.

Fig. 3 shows superimposed plots of the magnetodielectric response and the square of the magnetization measured at 17 K; the magnetodielectric response is symmetric here. The response scales with the square of the magnetization. This suggests that the magnetodielectric coupling originates from the P^2M^2 term in the free energy expansion, which is always allowed by symmetry in ferroelectromagnetic materials [11]. Nevertheless, the magnetodielectric effect in $MnCr_2O_4$ is much smaller compared to other multiferroics such as $TbMnO_3$, which has a magnetocapacitance of ~10%, even though the ferroelectricity in $MnCr_2O_4$ is also induced

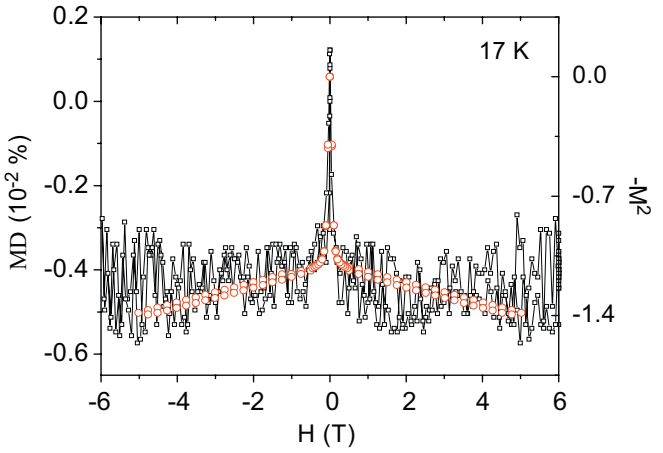

Fig. 3. Superimposed plots of the magnetodielectric response and the square of the magnetization of $MnCr_2O_4$ at 17 K.

by the magnetic structure. This result indicates that improper ferroelectricity, such as ferroelectricity induced by the magnetic structure, is no guarantee of obtaining a large magnetodielectric effect.

4. Summary

We have investigated the magnetic and dielectric properties of polycrystalline samples of the spinel $MnCr_2O_4$. Both the magnetization and dielectric measurements resemble those of single-crystal samples [5], which is in contrast to a previous report of polycrystalline $CoCr_2O_4$ [6], for which the properties are sample dependent. The suppression of the dielectric anomaly at T_f indicates that the correlation length of the conical magnetic structure increases with applied magnetic field. In the region between T_s and T_f, $MnCr_2O_4$ exhibits symmetric magnetocapacitance that scales with the square of the magnetization. Thus, the magnetodielectric coupling in this state appears to originate from the P^2M^2 term in the free energy. The magnetocapacitance becomes asymmetric with respect to field below T_f.

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