Pressure effect on magnetism and multiferroicity in Mn_2GeO_4

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The effect of high pressure exceeding 6 GPa on magnetism and multiferroicity was investigated for the olivine Mn_2GeO_4 that shows successive magnetic transitions at ambient pressure and a ferroelectric ground state driven by spin-spiral order. We measured heat capacity, dielectric constant, and electric polarization at various pressures using a diamond anvil cell. The pressure evolution of the magnetic structures was also investigated by powder neutron diffraction measurements using a Paris-Edinburgh press. We found that all of the magnetic transition temperatures are enhanced monotonically by applying pressure. Furthermore, the spin-driven ferroelectricity persists up to about 6 GPa but suddenly vanishes by 6.3 GPa. A consistent description of all data is achieved if an incommensurate-commensurate phase transition occurs with pressurization and causes the suppression of ferroelectricity. We discuss the origin of the observed pressure effects on the magnetism and multiferroicity in Mn_2GeO_4 in terms of a pressure-induced change in the superexchange magnetic interactions.

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I. INTRODUCTION

Olivine is a name for a series of minerals with the chemical formula A_2BO_4 ($A = \text{Fe, Mg, Ca, Mn, Co, or Ni}$; $B = \text{Si or Ge}$) that have long been investigated in the field of geoscience, for example, in terms of the effects of high pressure [1–3]. Most of the previous pressure studies on olivine compounds focused on pressure-driven structural transformations at or above room temperature (T). For example, it has been reported that olivine Mn_2GeO_4 (MGO), which has a $Pnma$ orthorhombic structure at ambient pressure (shown in Fig. 1), exhibits the sequence of pressure-induced structural transformations, olivine type $\rightarrow$ modified spinel type $\rightarrow$ strontium plumbate type above room T [4,5]. So far, however, there have been only a few studies of the high-pressure effect on the electronic properties of the olivine compounds below room T [6].

In the past several years, some of the olivine compounds have attracted the interest of condensed matter physicists due to their electronic properties, such as magnetism [7,8]. Recently, it was found that MGO exhibits three antiferromagnetic (AFM) phases at zero magnetic ($\mu_0 H$) field that occupy the following T regions; $T_{N1} = 47 \text{ K} > \text{AFM1} > T_{N2} = 17 \text{ K} > \text{AFM2} > T_{N3} = 5.5 \text{ K} > \text{AFM3}$ at ambient pressure [9,10]. In the AFM1 phase, magnetic Mn^{2+} moments are aligned primarily along the a axis but are slightly canted along the c axis, which gives rise to weak ferromagnetism. In the AFM2 phase, through a spin reorientation process, the moments are oriented nearly along the b axis, and no net magnetization appears in any direction. The final transition is into the AFM3 phase that displays a remarkably rare multiferroic property; both spontaneous magnetization and electric polarization develop along the c axis, simultaneously.

The spontaneous magnetization originates from a small canting of a commensurate (C) magnetic structure, while the ferroelectricity arises from the formation of an incommensurate (IC) spin-spiral structure. Our earlier experiments showed that the C and the IC magnetic structure components coexist and are superposed to form an elaborate multicomponent structure below the single transition temperature at T_{N3} [9]. It is also worth mentioning that MGO is the first spin-spiral-driven multiferroic discovered to display both spontaneous magnetization and electric polarization in the same direction.

In this paper, we report pressure effects on the microscopic magnetism and the spin-driven ferroelectricity in the multiferroic olivine-type MGO. Recently, there have been several high-pressure studies on spin-driven multiferroics from both experimental and theoretical perspectives [11–14]. For example, the pressure-induced reversal of ferroelectric polarization was found in YMn_2O_5 [12], and room- T multiferroicity was theoretically predicted in CuO under high pressure [13]. These studies show that the application of high pressure on spin-driven multiferroics is an effective way to both tune multiferroic phase transitions and to possibly explore new phases. Such measurements can also be expected to shed important light on the multiferroic mechanism, where for MGO, it must also describe the coupling between ferromagnetism and ferroelectricity. In our experiments, we have investigated the bulk dielectric properties and microscopic magnetic structures under high pressures exceeding 6 GPa. From our results, we discuss the evolution of the relationship between multiferroicity and the Mn-O-Mn superexchange interactions through the continuous tuning of the crystallographic structure under externally applied pressure.

II. EXPERIMENTAL DETAILS

Single crystals of MGO were grown by the floating zone technique [10]. The obtained crystals were cut into

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FIG. 1. (Color online) A schematic of the crystal structure of MGO, Ge ions are omitted for clarity. Five important Mn-O-Mn superexchange interaction paths are shown: two intrachain superexchange interactions γ and γ' and three interchain interactions α , α' , and α'' . Black solid lines marking Mn1-O1-Mn1 and Mn1-O2-Mn1 paths denote the intrachain superexchange interactions γ , and gray solid lines marking Mn1-O1-Mn2 and Mn1-O3-Mn2 paths denote the intrachain interactions γ' . The green dashed line connecting Mn2-O3-Mn2 shows the interchain superexchange interaction α , the gray dashed line connecting Mn1-O2-Mn2 shows the interchain interaction α' , and the black dashed line connecting Mn1-O3-Mn2 shows the interchain interaction α'' . The bond angles of γ and γ' are near the right angle; thus, these intrachain superexchange interactions are expected to be weaker than the interchain superexchange interactions α , α' , and α'' with bond angles of about 130° .

thin plate-shaped specimens with dimensions of typically $\approx 200 \times 230 \times 25 \mu\text{m}^3$ and the widest faces perpendicular to the c axis. Measurements of heat capacity by ac calorimetry (C_{ac}), dielectric constant along the c axis (ϵ_c), and electric polarization along the c axis (P_c) in applied pressures up to $p \approx 6.5$ GPa were carried out using a diamond anvil cell (DAC). The specimen was loaded into the DAC with an 800- μm culet diameter diamond anvil. Glycerin was used as the pressure-transmitting medium. A microscope image of the specimen setup in the pressure chamber and observed through the diamond anvil is shown in the inset of Fig. 2(a). Further details of the experimental techniques are reported in Refs. [14–16]. The DAC was introduced into a commercial Physical Property Measurement System (Quantum Design), and we conducted measurements of C_{ac} , ϵ_c , and P_c at various T , pressures, and $\mu_0 H$ fields were carried out. By using a lock-in amplifier, an LCR meter, and an electrometer, C_{ac} , ϵ_c , and P_c were measured, respectively. Both electric (E) and $\mu_0 H$ fields were applied only along the ferromagnetic and ferroelectric c axis. Before and after the respective measurements, applied pressure was determined by a ruby fluorescence method at both room T and 10 K. Measurements of the electric polarization under high pressure using a DAC were recently carried out on multiferroic CuCrO_2 , which displays a spontaneous polarization of $\approx 10^2 \mu\text{C}/\text{m}^2$ [14]. In the present study, we successfully measured the high-pressure dependence of the electric polarization of MGO, which is ten times smaller than that of CuCrO_2 measured previously.

To study the magnetic structures as a function of both T and applied pressure, we conducted powder neutron diffraction (PND) measurements. These measurements were carried out

FIG. 2. (Color online) T profiles of (a) C_{ac} and (b) ϵ_c measured at selected pressures. Black inverted triangles show phase transition points. Inset of (a): microscope image of MGO with four measurement wires and inside the pressure chamber. Inset of (b): a magnified view of ϵ_c at 4.7, 5.9, and 6.3 GPa in the T range from 7 to 11 K. The respective data are vertically offset for clear comparison.

using the cold neutron powder diffractometer DMC at the Swiss Spallation Neutron Source (SINQ), Paul Scherrer Institute (PSI), Switzerland. The wavelength of the neutron beam was $2.457 \text{ \AA}$, and the sample pressure was applied using opposed anvil techniques and a Paris-Edinburgh VX 5 press (details of the experimental setup are described elsewhere [17,18]). A powder sample of MGO was prepared by crushing a single crystal, and it was subsequently loaded into a TiZr gasket. The pressure-transmitting medium was a mixture of deuterated methanol and ethanol with a 4:1 volume ratio. The estimated powder sample volume was 50 mm^3 . The applied pressures were estimated by measuring the change in the unit cell volume of MGO under pressure and using the third-order Birch-Murnaghan equation of state [19,20], with the obtained bulk modulus B at each T and ambient pressure (we adopted the pressure derivative of B , $B' = 4.4$, as reported for a sister compound, Mg_2SiO_4 [21]). The crystal and magnetic structure refinements were carried out with the use of FullProf [22].

III. RESULTS AND DISCUSSION

Figure 2(a) shows the T dependence of the heat capacity C_{ac} measured at selected pressures. All the data shown in Fig. 2 were taken upon the heating process. Each C_{ac} - T curve

displays a classical λ -type anomaly at the T_{N1} transition and two further narrow peak structures at T_{N2} and T_{N3} that are typical of first-order phase transitions. We mention here that under high pressure, there remains just a single transition temperature T_{N3} . This strongly suggests that the IC + C magnetic structure does not become phase separated with increasing pressure and that the phase is not a magnetic domain composed of separate IC and C structures but instead one that corresponds to just a single magnetic structure.

Figure 2(b) displays the T profiles of ε_c measured at 100 kHz, and under various pressures. The inset of Fig. 2(b) shows a magnified view of the data at 4.7, 5.9, and 6.3 GPa around T_{N3} . Accompanied by the anomalies in C_{ac} observed at T_{N1} , T_{N2} , and T_{N3} , the ε_c - T curves also exhibit anomalies at the respective transition temperatures. The steplike anomalies at T_{N3} correspond to the transition into the multiferroic phase with the multicomponent magnetic structure. From inspection, it is clear that all phase transition temperatures become enhanced monotonically with increasing pressure. According to the thermal expansion data obtained with a strain gauge method reported in Ref. [10], the unit cell volume of MGO increases monotonically with increasing T and shows two stepwise jumps at T_{N2} and T_{N3} that are symptomatic of first-order transitions. From the Clausius-Clapeyron relation

$$\frac{\partial p}{\partial T} = \frac{L}{T(V_{\text{high}} - V_{\text{low}})},$$

where L is the specific latent heat, V_{high} and V_{low} are, respectively, the specific volumes of the high- T and low- T phase, the specific volume change at each phase transition $V_{\text{high}} - V_{\text{low}}$ is positive, and then $\partial p / \partial T > 0$. This supports the observed monotonic enhancement of T_{N2} and T_{N3} by applying pressure. The behavior of $\partial p / \partial T$ at the second-order phase transition temperature T_{N1} can be discussed from the point of view of the Ehrenfest equation

$$\frac{\partial p}{\partial T} = \frac{\Delta C_p}{TV\Delta\beta},$$

where C_p is the isobaric specific heat and β is the coefficient of thermal expansion. Since both ΔC_p [Fig. 2(a)] and $\Delta\beta$ [10] are negative at T_{N1} , $\partial p / \partial T > 0$. This is consistent with the observed pressure-induced monotonic enhancement of T_{N1} . Moreover, the behavior can be qualitatively explained as resulting from the contraction of the Mn-O bond lengths with applied pressure. Indeed, the shortening of A-O bond lengths by applied pressure has been observed in the sister compound Fe_2SiO_4 [23]. The shortening of bond lengths, especially the interchain Mn2-O bonds (see Fig. 1), enhances the superexchange interactions and stabilizes the magnetically ordered states.

Figures 3(a) and 3(b), respectively, display the T profiles of pyroelectric current and electric polarization along the c axis (P_c) under selected pressures. Prior to each of the respective measurements, we cooled the specimen at $E = 2$ MV/m and $\mu_0 H = 1$ T applied along the c axis from a T above T_{N3} [magnetoelectric (ME) cooling]. All the data shown in Fig. 3 were taken upon warming runs and heating at a rate of 10 K/min after the ME cooling procedure. Figure 3(b) shows that the value of P_c at the lowest T stays constant up to 5.9 GPa and suddenly drops to zero at 6.3 GPa. In addition, as shown

FIG. 3. (Color online) T profiles of (a) pyroelectric current along the c axis and (b) P_c measured at 1 T under various pressures. E and $\mu_0 H$ fields were applied parallel to the c axis. These data were taken upon sweeping T up at a rate of 10 K/min.

in Fig. 3(a), the peak observed in the pyroelectric current broadens and vanishes with increasing pressure. A similar observation can be made for the T dependence of ε_c [inset of Fig. 2(b)]. The steplike anomaly of ε_c changes to a cusplike one at 6.3 GPa, which indicates T_{N3} to remain. Overall, these results demonstrate a ferroelectric-to-paraelectric phase transition to occur in the lowest T phase through the application of high pressure above about 6 GPa. Since the ferroelectricity in MGO is generated by the IC component of the magnetic order, we expect that the IC magnetic structure vanishes with the increase of externally applied pressure. From this viewpoint, we propose that the pressure effect acts to resolve the magnetic frustration that causes the IC spiral order.

To examine the magnetic structure in each phase, we performed PND measurements at several pressures. The measurements were performed at selected T s after the pressurizing process at ~ 120 K ($> T_{N1}$) and at which the methanol:ethanol pressure-transmitting medium is much softer than MGO. Figure 4 shows PND profiles at 80 K [paramagnetic phase, (PM)], 20 K (AFM1), 10 K (AFM2), and 4.5 K (AFM3) under a pressure of 1 GPa. Due to the small sample volume inherent to such high-pressure neutron measurements, full refinements of the magnetic and crystal structures are not possible from the data. However, the difference between the PM (AFM1) and the AFM1 (AFM2) phases in the PND profiles is characterized by the absence or presence of $\{110\}$ and $\{001\}$ (strong $\{100\}$ and $\{300\}$) magnetic Bragg peaks indicated by cross marks (square symbols). Furthermore, by focusing on the IC magnetic Bragg peaks (star symbols), we can distinguish the profiles due to the AFM2 and the AFM3 phases. By this approach, we identify the magnetic phase at each T and under various pressures.

FIG. 4. (Color online) PND profiles measured at 80, 20, 10, and 4.5 K under a pressure of 1 GPa. Numbers listed below the profiles denote general hkl indices of the respective magnetic Bragg peaks. Dot symbols and black lines represent observed data points and Le Bail fits, respectively. Cross marks denote 110 and 001 magnetic Bragg peaks, while square symbols show 100 and 300 peaks. Star symbols denote peaks due to the IC structure. The respective data are vertically offset for clear comparison.

Figure 5 shows the profiles at 4.5 K in the AFM3 multiferroic phase under pressures of 1.0, 2.7, and 5.1 GPa. With increasing pressure, the IC peaks indicated by inverted triangles shift toward the C peaks, merge into the C peaks, and then are not clearly observed at 5.1 GPa. In combination with the discussion of the ferroelectric-to-paraelectric phase transition above, the PND result supports the expectation that an IC-C phase transition occurs in the lowest T phase under the application of high pressure. There is no clear evidence for a change in the ambient pressure $Pnma$ crystal symmetry for the pressures studied here, so we can, indeed, conduct a discussion of the

FIG. 5. (Color online) PND profiles measured at 4.5 K under pressures of 1.0, 2.7, and 5.1 GPa. Dot symbols and black lines represent observed data points and Le Bail fits, respectively. Blue triangles denote peaks due to the IC structure. The respective data are vertically offset for clear comparison.

magnetic properties in terms of the irreducible representations for the magnetic structures derived within the space group $Pnma$.

Concerning the origin of the IC-C (ferroelectric-paraelectric) transition, we suggest two general scenarios that are consistent with the present data. According to a symmetry analysis, the irreducible representations of the C structure and the irreducible corepresentations of the IC structure in the AFM3 multiferroic phase are $\Gamma_C^1 + \Gamma_C^3$ and $D_{IC}^1 + iD_{IC}^2$, respectively (details of the analysis are shown in [9]). Since the combination of $\Gamma_C^1 + \Gamma_C^3$ is nonpolar, the first scenario is that the IC structure simply vanishes; thus, a phase transition from an IC + C multicomponent structure to a C structure occurs. A second scenario is that the IC structure component transforms into a different type of C structure (that we call C'), which is itself both noncentrosymmetric and nonpolar. This is thereby a transition from an IC + C structure to a C' + C structure.

For the first scenario, the pressure-induced transition could be first-order in character, if the two IC order parameters disappear simultaneously. This would be manifested by the sudden vanishing of the IC magnetic peaks at a certain pressure. Alternatively, a sequential suppression of IC order parameters could be manifested as a series of pressure-driven second-order phase transitions, which leads to a more gradual reduction of the IC peak intensity. This could also be the case for the second scenario, if the applied pressure leads to a smooth change in symmetry of the original IC order parameters. In this latter case, by neutron diffraction we could observe the change of IC peak positions to C positions having fractional indices under high pressure. Although the pressure dependence of the IC peaks is not clear from the present PND results, resolving the nature of the pressure-induced transition is of great interest and can be tackled by future high-pressure neutron diffraction experiments on single-crystal samples.

The previously described experimental results on the pressure dependence of the magnetic and ferroelectric properties of MGO are summarized in the p - T phase diagram shown in Fig. 6. The phase boundaries are determined by the T profiles of C_{ac} (open circle symbols) and ϵ_c (open triangle symbols). The ferroelectric phase is denoted by the shaded area in the phase diagram.

The pressure dependence of the magnetic transition temperature T_{N1} can be analyzed in the framework of the so called Bloch power law model [24] that has been employed to describe numerous ferromagnetic and AFM systems [25–27]. According to the model, the magnitude of superexchange interactions varies as a function of the $-10/3$ power of the volume V , or the tenth power of an interionic distance, which is frequently expressed in terms of a magnetic Grüneisen parameter $\Gamma \equiv -d \ln T_{N1} / d \ln V$. From the data of Fig. 6, we obtain $d \ln T_{N1} / dp = 0.046 \pm 0.003 \text{ GPa}^{-1}$ and

$$\Gamma = \frac{d \ln T_{N1}}{d \ln V} = B \frac{d \ln T_{N1}}{dp} = 5.0 \pm 0.3, \quad (1)$$

using the bulk modulus $B \approx 110.2 \text{ GPa}$ that is obtained from the PND data at 50 K and at ambient pressure. The value obtained by Eq. (1) is different from $10/3$ (≈ 3.3), which is expected from the Bloch power law model, and is similar to that found for Fe_2SiO_4 ($\approx 4.2 \pm 0.4$) [6]. In the olivine compounds,

FIG. 6. (Color online) Pressure- T phase diagram of MGO. Circle and triangle symbols represent data obtained by measurements of heat capacity and dielectric constant, respectively. A shaded area shows the phase where ferroelectricity exists. A black line is a fit to the T_{N1} points and is described by the formula that pressure is proportional to $\ln T_{N1}$ (see text for details). Closed symbols denote p - T points, where PND measurements were conducted; green, red, and blue symbols show the magnetic structures in the AFM1, AFM2, and AFM3 phases, respectively. The filled black symbol in the lowest phase at 5.1 GPa denotes a PND measurement where a C magnetic structure was observed in the AFM3 phase, but the IC structure was not (see Fig. 5).

such as MGO, there are five principal types of exchange interactions: two intrachain superexchange interactions γ and γ' , and three interchain interactions α , α' , and α'' (see Fig. 1). These superexchange interactions will depend on not only the bond lengths but also the bond angles as the system is pressurized (similar behavior is observed in Fe_2SiO_4 according to Ref. [23]). This indicates that the pressure effect on the intrachain interactions expected by shortening the bond lengths will be somewhat alleviated by slight changes in the bond angles. Furthermore, the intrachain interactions corresponding to Mn-O-Mn bond angles close to 90° can be reasonably expected to be weaker than the interchain ones according to the Goodenough-Kanamori rules [28,29]. Thus, the pressure effect on the intrachain interactions may be different from that on the superexchange interactions in MnF_2 (Mn-F-Mn $\approx 128^\circ$) [25] and FeF_2 (Fe-F-Fe $\approx 128^\circ$) [26] in which the pressure dependence of T_N is well explained by Bloch's law. Although the law is often applied to describe the pressure dependence of a transition temperature in various magnetic systems, we cannot simply discuss the effects by applying the law to the present olivine system. Progress towards a more accurate description of the pressure-driven enhancement of T_N could be facilitated by careful high-pressure measurements of the magnetic superexchange interactions.

IV. CONCLUSIONS

We have investigated the effect of applied pressure on magnetism and multiferroicity in olivine-type MGO that shows successive magnetic transitions as a function of T at ambient pressure and a ferroelectric ground state driven by an IC spin-spiral order. From the results of heat capacity measurements, it was found that all the magnetic transition temperatures increase monotonically with increasing pressure. In particular, the first magnetic ordering temperature T_{N1} increases with pressure linearly at the rate of $dT_{N1}/dp = 0.046 \pm 0.003 \text{ GPa}^{-1}$. The pressure dependence of T_{N1} can be partly explained in terms of a classical Heisenberg exchange Hamiltonian model on the assumption that the size of the superexchange interactions scale proportionally with the $-10/3$ power of the volume.

It was also found that the spin-driven ferroelectricity vanishes suddenly at around 6 GPa. To further clarify the origin of the pressure effect, we carried out measurements of PND under high-pressure conditions and examined the evolution of magnetic structures. The IC magnetic Bragg peaks shift toward C positions with pressurization. All of these results suggest an IC-C phase transition to occur under high pressure, and the suppression of the spin-driven ferroelectricity occurs at this transition. We explain the observed pressure effects from the viewpoint of superexchange interactions, though a full description requires further careful high-pressure experiments.

The present results unequivocally demonstrate the application of pressure to be an effective perturbation for tuning the multiferroic properties of MGO and that the IC ground state at ambient pressure becomes unstable at a purely C state under high pressure. In addition, in the present study, we succeeded in measuring a remarkably small magnitude of electric polarization ($\approx 10^1 \mu\text{C}/\text{m}^2$) due to spin-driven ferroelectricity under high-pressure conditions exceeding 6 GPa.

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