Low-temperature dielectric anomalies in HoMnO_3 : The complex phase diagram

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The dielectric constant of multiferroic hexagonal HoMnO_3 exhibits an unprecedented diversity of anomalies at low temperatures ($1.8 \text{ K} < T < 10 \text{ K}$) and under external magnetic fields related to magnetic phase transitions in the coupled system of Ho moments, Mn spins, and ferroelectric polarization. The derived phase diagram is far more complex than previously assumed including reentrant phases, phase transitions with distinct thermal and field hysteresis, as well as several multicritical points. Magnetoelastic interactions introduce lattice anomalies at the magnetic phase transitions. The reevaluation of the T - H phase diagram of HoMnO_3 is demanded.

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Among the multiferroic compounds hexagonal rare-earth manganites, RMnO_3 ($R = \text{Sc, Y, Ho to Lu}$), have attracted recent attention because of the coexistence of antiferromagnetic (AFM) and ferroelectric (FE) orders below their Néel temperatures, $T_N < 100 \text{ K}$. The mutual interference and the possible correlation of magnetic and ferroelectric orders are of fundamental interest and of significance for prospective applications. Since the report¹ of a dielectric anomaly at T_N of YMnO_3 and later observations of similar effects in other hexagonal RMnO_3 the origin of the magnetodielectric coupling in these compounds has been a matter of discussion.²⁻⁵ In the magnetic symmetries realized just below T_N the direct coupling between the in-plane staggered AFM magnetization and the c -axis FE polarization is not allowed.⁶ The indirect coupling via lattice strain or other secondary effects has therefore been proposed.⁵ In fact, the existence of strong spin-phonon interactions was concluded from the anomalous temperature dependence of the thermal conductivity⁷ and the thermal expansion anomalies observed at T_N of HoMnO_3 .⁸

The magnetic order below 100 K is very complex for some RMnO_3 and it is determined by the strong in-plane AFM superexchange interaction of the Mn^{3+} spins and their geometric frustration in the $P6_3cm$ hexagonal structure. While strong in-plane magnetic correlations exist well above the Néel temperature^{8,9} the long-range AFM order of the Mn^{3+} sets in only below 100 K with a frustrated, noncollinear spin arrangement (neighboring moments form an angle of 120°). The different spin arrangements and magnetic symmetries compatible with the $P6_3cm$ crystalline structure have been discussed in detail by Fiebig *et al.*¹⁰ The direct magnetic exchange of the R^{3+} ions, essential at low temperatures, and the coupling of the rare-earth moments with the Mn spins as well as the FE polarization gives rise to a wealth of interesting physical phenomena and a complex magnetic phase diagram. Several subsequent magnetic phase changes have been observed in HoMnO_3 below $T_N = 76 \text{ K}$, including a sharp Mn spin-rotation transition at $T_{SR} = 33 \text{ K}$ with the onset of AFM Ho-moment order and another transition at about 5 K involving a major increase of the Ho^{3+} moments.^{4,10-13} Different magnetic symmetries partially coexisting below T_N have also been reported for LuMnO_3 and ScMnO_3 .¹³

Under applied magnetic fields, HoMnO_3 exhibits the most complex T - H phase diagram of all hexagonal RMnO_3 with several field-induced reentrant phases and transitions at low temperatures.^{10,14} Recent neutron scattering experiments have suggested an even higher degree of phase complexity at low T and the existence of an unusual pentacritical point at about 6 K and 13 kOe .¹⁵ Distinct anomalies of the dielectric constant ϵ have been observed at the zero field transitions, notably a sharp peak of $\epsilon(T)$ at T_{SR} that defines a new reentrant phase.⁵ This phase was shown to extend over a broader range in the T - H phase diagram^{5,14} and it was confirmed by neutron scattering experiments.¹⁵ Whereas the previous dielectric investigation was limited to temperatures above 7 K , alternative measurements of magnetization and heat capacity have revealed additional phase boundaries in the (low T)-(low H) region of the phase diagram that are distinctly different from the phase lines derived from neutron scattering.¹⁵

In order to unambiguously identify the various phase boundaries and to resolve the complex phase diagram of HoMnO_3 we have extended the investigation of the dielectric properties to low temperatures ($T > 1.8 \text{ K}$) and high magnetic fields ($H < 70 \text{ kOe}$). The dielectric constant as a function of temperature and magnetic field exhibits sharp anomalies at all magnetic phase transitions due to the strong magnetodielectric coupling in the compound. New phase transitions are detected at low temperatures demanding the reevaluation of the phase diagram and the exploration of the magnetic structures by alternative experimental methods.

Single crystals of HoMnO_3 of typical size $3 \times 5 \times 0.1 \text{ mm}^3$ were synthesized as described elsewhere.¹⁴ The capacitance was measured with the electric field directed along the hexagonal c axis employing the high precision capacitance bridge AH 2500A (Andeen Hagerling) operating at a 1-kHz frequency. The physical property measurement system (Quantum Design) was used to control the temperature and magnetic field (parallel to the c axis).

The dielectric constant below 100 K at zero magnetic field exhibits three distinct anomalies associated with the known magnetic transitions of HoMnO_3 .^{5,10,12,14,16} The low-temperature anomaly of $\epsilon(T)$ at $T_2 = 5.2 \text{ K}$ and its magnetic

FIG. 1. (Color online) Low-temperature dielectric constant, $\epsilon(T)$ at different magnetic fields. For better clarity, the curves are vertically offset and the base line for each curve is shown by the dotted line with the magnetic field value as a label. The phase boundaries and anomalies discussed in the text are indicated by dotted lines labeled as T_i and $\tilde{T}_j$.

field dependence is shown in Fig. 1. The sharp rise at T_2 is followed by a continuous decrease of $\epsilon(T)$ to lower T . The small hump at 4.9 K [denoted by $\tilde{T}_1$ and the dotted line in Fig. 1(a)] indicates another subtle change in the magnetic structure. A second small peak of the specific heat was observed at the same temperature.¹⁴ Therefore, the low-temperature magnetic transition of HoMnO₃ appears to proceed in two subsequent steps, only 0.3 K spaced apart. Neutron scattering experiments suggest a major increase of the Ho magnetic moments at this temperature while the Mn spins rotate another time by 90°.¹² These scattering measurements, however, do not have the temperature resolution to separate the two transitions that are unambiguously shown in the data of Fig. 1(a). The two anomalies of $\epsilon(T)$ separate in external magnetic fields and $\tilde{T}_1$ [dotted line in Fig. 1(a)] is unambiguously determined up to about 14 kOe by the change of slope of $\epsilon(T)$. It also corresponds to a similar feature observed in the low-temperature specific heat.¹⁴

Above 5 kOe a third anomaly of $\epsilon(T)$ arises at low T in form of a sharp increase, as shown in Fig. 1(a). The temperature of this anomaly, $T_3(H)$, increases with H and passes through a maximum at about 3.3 K and 12 kOe. $T_3(H)$ is in perfect agreement with the sharp peak of the ac magnetic susceptibility and the specific heat reported by us before.¹⁴ All data have been acquired upon decreasing and increasing

temperature. No thermal hysteresis was observed at the transitions (T_2 , $\tilde{T}_1$, and T_3) for $H < 10$ kOe. At 11 kOe, however, a narrow hysteresis is evidenced near 6 K [Fig. 1(a)]. With further increasing H a small steplike anomaly of $\epsilon(T)$ splits off from the drop of ϵ at T_2 and shifts to lower T with increasing field [Fig. 1(b)]. We denote the critical temperature of this new phase boundary by $T_5(H)$. The phase change at T_5 is clearly associated with a thermal hysteresis that broadens with increasing H . Above 15 kOe the exact value of T_5 is difficult to extract from $\epsilon(T)$ because of the large hysteresis. Between 15 and 18 kOe the transition is only observed upon heating whereas with cooling the phase changes directly into the low temperature phase (LT1) at $T_3 \approx 3.2$ K, as indicated by the arrows attached to the 16 kOe data in Fig. 1(b). The exact values of $T_5(H)$ and the width of the hysteresis associated with T_5 were more accurately derived from isothermal $\epsilon(H)$ scans.¹⁷ Above 18 kOe a distinct peak of $\epsilon(T)$ arises at about 2.8 K (18.7 kOe), which is consistent with a similar peak of the ac magnetic susceptibility.¹⁴ The position of this peak, shown in Figs. 1(b) and 1(c) [denoted by $\tilde{T}_3(H)$], moves to higher T with increasing field. The peak of $\epsilon(T)$ broadens with increasing H and it becomes less well resolved at fields exceeding 28 kOe [Fig. 1(c)]. At 22 kOe two additional steps of $\epsilon(T)$ appear below 2.5 K indicating other sharp transitions in the phase diagram of HoMnO₃.

FIG. 2. (Color online) Low-temperature phase diagram of HoMnO_3 . Phase boundaries T_1 to T_5 are drawn as solid lines. The closed and open symbols are derived from $\varepsilon(T)$ and $\varepsilon(H)$, respectively. Additional anomalies $\tilde{T}_1$ to $\tilde{T}_3$ are indicated by dashed lines. The shaded areas mark regions in the phase diagram where hysteresis effects have been observed.

One of these transitions coincides with the $T_1(H)$ phase boundary separating the intermediate (INT) and the high-temperature (HT1) phases as determined from ac susceptibility¹⁴ and high- T dielectric measurements.⁵ The other sudden change of $\varepsilon(T)$, denoted by $T_4(H)$ in Figs. 1(c) and 1(d) can be followed to the highest magnetic fields of 70 kOe and it is obviously related to the transition into the LT2 phase (the AFM- A_1 phase in the notation of Fiebig *et al.*).^{10,14} It is remarkable that this transition is very sharp and does not show indications of thermal hysteresis in contrast to conclusions from optical experiments.¹⁰ T_4 first increases from $H=22$ kOe, passes through a maximum at 52 kOe and 4.6 K, and decreases again at a higher magnetic field [Figs. 1(c) and 1(d)]. $T_1(H)$ and $T_4(H)$ seem to merge at low temperatures close to 20 kOe.

The various phase boundaries have been investigated in more detail by isothermal measurements of ε as a function of the magnetic field.¹⁷ The isothermal $\varepsilon(H)$ displays similar anomalies as $\varepsilon(T)$ and allows to determine the phase boundary $T_5(H)$ and the hysteretic regions in the phase diagram more precisely. The data are included as open symbols in Fig. 2. In addition to the anomalies of $\varepsilon(T)$ discussed above, a broader maximum of $\varepsilon(H)$ appears below 12 kOe between 3.2 and 4.8 K. This maximum of $\varepsilon(H)$, shown as the dashed line $\tilde{T}_2$ in Fig. 2, may not represent another phase boundary but it indicates a smooth change of the magnetic structure in this region of the phase diagram.

The dielectric anomalies observed in the T and H dependence of ε are closely correlated with similar anomalies of the ac magnetic susceptibility χ_{ac} .¹⁴ The similarities include the enhancement of both susceptibilities in the INT phase, the remarkable peak at $\tilde{T}_3(H)$, the broad peak along $\tilde{T}_2(H)$, and the sharp changes in crossing the $T_1(H)$, $T_2(H)$, and $T_3(H)$ phase boundaries. The common features of ε and χ_{ac} prove the existence and the strength of the magnetodielectric

coupling in HoMnO_3 at low T . Due to this coupling the magnetic phase diagram is completely determined by the anomalies of ε as shown above and summarized in Fig. 2.

The multitude of anomalies observed in HoMnO_3 by magnetic, thermodynamic, dielectric, as well as optical and neutron scattering experiments makes it difficult to unambiguously identify the various phases and transition lines. A systematic approach appears necessary to reconcile all data correctly. Based on the sharp, steplike changes of ε we have identified five phase boundaries denoted by $T_1(H)$ to $T_5(H)$ (solid lines with symbols in Fig. 2). Other remarkable features of $\varepsilon(T, H)$, such as narrow or broader peaks and the change of slope of $\varepsilon(T)$ denoted by $\tilde{T}_1$ to $\tilde{T}_3$, are shown as dashed lines in Fig. 2. Currently it is not clear if the latter anomalies define true phase boundaries but they indicate subtle changes of the magnetic structure. In order to resolve the different phase boundaries in the very complex (low T)-(low H) region we approach this part of the phase diagram from a high temperature or high magnetic field where the magnetic phases are well defined. Including the magnetic and thermodynamic anomalies,¹⁴ the phase boundaries can be unambiguously traced to lower T and H .

$T_1(H)$ and $T_2(H)$ define the transitions between the HT1 and HT2 phases including the intermediate INT phase. T_1 is clearly defined by the sharp drop of ε and χ_{ac} and it can be traced from 33 K ($H=0$) to about 2.5 K (22 kOe), where it merges with T_4 . $T_2(H)$ is uniquely determined by the sharp increase of ε , χ_{ac} , and the heat capacity¹⁴ and it stretches from (33 K, $H=0$) to (20 K, 34 kOe) and back to (5.2 K, $H=0$), as shown in Fig. 2. The dome-shaped LT1 phase and its phase boundary $T_3(H)$ are unambiguously defined by the step of $\varepsilon(T, H)$, as well as by the narrow peaks of $\chi_{ac}(T, H)$ and the heat capacity.¹⁴ $T_5(H)$ connecting the T_1 and T_3 phase boundaries near 15 kOe is clearly identified by the small step of $\varepsilon(T)$ and its associated hysteresis. Similar features have been observed in χ_{ac} .¹⁷ The remaining phase boundary between the HT1 and LT2 phases, $T_4(H)$, was not well characterized before because of hysteresis effects observed in optical experiments¹⁰ or due to broad changes of the magnetization.¹⁴ The dielectric data, however, prove that this phase transition is sharp and no hysteresis was observed. T_4 defines another dome-shaped phase with a maximum of 4.6 K at 52 kOe. The weaker anomalies of $\varepsilon(T, H)$ labeled $\tilde{T}_1$ to $\tilde{T}_3$ (dashed lines in Fig. 2) will be discussed elsewhere.¹⁷

The phase boundaries T_1 to T_5 include several multicritical points. Two tricritical points are located at the intersection of $T_5(H)$ with $T_2(H)$ and $T_3(H)$. Of particular interest is the region near 20 kOe and below 3 K. T_1 and T_4 come close and could form another tricritical point. However, $T_3(H)$ is also very close and there is the possibility that all three transition lines merge at lower T , possibly at $T=0$. This would result in a tetracritical point at or close to zero temperature, an unusual phenomenon of considerable interest. Investigations at ultralow temperatures are therefore desired to elucidate this remarkable T - H region of the phase diagram.

The phase diagram summarized in Fig. 2 is to be compared with the recent conclusions from neutron scattering

FIG. 3. (Color online) Magnetic field dependence of the c -axis length at various temperatures. Clear anomalies are observed at the transition temperatures T_1 , T_2 , and T_3 . Different data sets are offset for clarity. The dotted line with the temperature value attached marks the $H=0$ value for each curve.

data.¹⁵ Although most of the anomalies observed in the scattering intensities can be accommodated by our phase diagram, the major phase boundaries are drawn differently, resulting in an unusual pentacritical point at about 6 K and 13 kOe.¹⁵ The main difference to our results is a hysteretic anomaly between 10 and 15 kOe derived from the (2,1,0) and (1,0,0) peak intensities that extends to lowest T . This anomaly appears to be the extension of the $T_3(H)$ phase boundary into the LT1 phase, however, we have not observed any anomaly of $\varepsilon(H)$ or $\chi_{ac}(H)$ below $T_3(H)$ between 5 and 20 kOe. The possible origin of this discrepancy could lie in the different geometries of the two experiments. ε and χ_{ac} have been measured with electric and magnetic fields along the c axis whereas the neutron scattering experiments do not include out-of-plane magnetic peaks.

The physical nature and the magnetic structures of the different phases revealed in Fig. 2 are not completely resolved. Neutron scattering^{12,16} and optical investigations¹⁰ have assigned the $P6_3cm$, $P6_3cm$, and $P6_3cm$ magnetic symmetries to HT1, HT2, and the phase below 5 K (enclosed by T_2 , T_5 , and T_3 in Fig. 2), respectively. For the INT phase we propose the lower $P6_3$ symmetry where the Mn spins form an angle φ_{Mn} between 0 and 90° with the a axis. We suggest that φ_{Mn} changes continuously as a function of T and H within the INT phase. The magnetic structures of the LT1 and LT2 phases are yet to be explored.

The intriguing similarity of magnetic and dielectric properties raises the question about the nature of their correlation. Strong magnetoelastic effects have recently been shown to exist in HoMnO_3 at $H=0$ and to be responsible for the magnetodielectric coupling at and below T_N .⁸ To investigate lattice anomalies in the low-temperature region of the phase diagram we have measured the c -axis length as a function of H for constant T between 1.8 and 20 K (Fig. 3) using the strain gauge method. At higher T 's [Fig. 3(a)] $c(H)$ shows a rapid increase with H between T_2 and T_1 in the INT phase. The corresponding slope changes of $c(H)$ coincide with the T_2 and T_1 phase boundaries of Fig. 2. The increase of the c axis with the transition from HT2 to HT1 is consistent with the zero field expansion measurements that showed an abrupt increase of the c -axis length with increasing T at T_{SR} .⁸ Below 5 K $c(H)$ is a more complex function [Fig. 3(b)]. The slope change at $T_1(H)$ becomes more pronounced and, below about 3 K, two sharp minima of $c(H)$ develop between 5 and 20 kOe. These two minima precisely trace the phase boundary $T_3(H)$ of Fig. 2. No other anomalies could be observed within the experimental resolution. $c(H)$ is constant in the LT2 phase ($H > 22$ kOe, $T < 3$ K), i.e., there is no c -axis magnetoelastic effect in this phase. The observed lattice anomalies prove the important role of the spin-lattice coupling at low temperatures in HoMnO_3 and they provide a possible explanation for the observed correlation of magnetic and dielectric properties and the complex T - H dependence of the dielectric constant.

In summary, the T - H phase diagram of HoMnO_3 is resolved via measurements of the dielectric constant. At least six different phases can be distinguished below T_N through sharp changes of $\varepsilon(T, H)$. Additional anomalies in form of a slope change of $\varepsilon(T)$ or distinct peaks of $\varepsilon(T, H)$ are monitored throughout the phase diagram. Several multicritical points are described and the possible existence of an unusual tetracritical point at zero temperature is proposed. The strong correlation of magnetic and dielectric properties with the lattice anomalies observed at the magnetic phase boundaries emphasize the role of magnetoelastic effects in promoting the magnetodielectric coupling in HoMnO_3 .

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