The search for and study of a coupling between the ferroelectric and magnetic orders in ferroelectromagnets, such as the hexagonal manganites, are of both fundamental and applied significance. This is because, by symmetry arguments, such a direct coupling in manganites is highly unlikely. However, it is not inconceivable that, through certain secondary indirect interactions, such a coupling exists and results in a magnetodielectric effect with an interesting device potential in which the dielectric (magnetic) properties can be modified by the onset of a magnetic (dielectric) transition or the application of a magnetic (electric) field. We have therefore examined the dielectric and magnetic properties of hexagonal HoMnO$_3$ single crystals as functions of temperature and magnetic field. Indeed, in the presence of a magnetic field below 4.1 T, we have detected a new reentrant phase in HoMnO$_3$ below its zero-field Mn-spin reorientation transition temperature of 32.8 K, indicative of a coupling between the magnetic and ferroelectric orders and introducing an additional dimension into the intriguing magnetic phase diagram of the compound.

The hexagonal manganites, R MnO$_3$ (R = Sc, Y, Er, Ho, Tm, Yb, Lu), have attracted attention because of a rich variety of antiferromagnetic (AFM) as well as ferroelectric (FE) phases with high FE Curie temperatures between 590 and 1000 K. The AFM order of the Mn spins and/or the R moments (e.g., Ho) is stabilized at lower temperature and coexists with the FE order. The Mn ions form a triangular lattice in which the moments are coupled antiferromagnetically by superexchange via the in-plane oxygen ions. This gives rise to spin-frustration effects and an AFM spin arrangement with neighboring spins rotated by 120°. The magnetic structures have been investigated by neutron scattering and second harmonic generation optical experiments [1–5].

Hexagonal HoMnO$_3$ is FE below 830 K and its Mn sublattices exhibit AFM order below $T_N = 76$ K. A sharp Mn-spin-reorientation transition from $P6_3$ to $P6_3$ magnetic symmetry takes place at $T_{SR} = 33$ K together with another Mn-spin reorientation close to 4 K. In $P6_3$ symmetry 1/3 of the Mn spins are aligned with the crystallographic a axis, whereas in the $P6_3$ phase the Mn spins are rotated in plane by 90°. The compound possesses a very interesting reentrant magnetic phase diagram [5]. In addition to the Mn-spin ordering, neutron scattering experiments suggested an AFM ordering of part of the Ho spins with the principal spin direction along the c axis below or close to $T_{SR}$ [2,3]. The AFM orders below $T_N$ clearly coexist with the FE order. Although the direct coupling between the in-plane staggered magnetization and the polarization is not allowed by symmetry [6], the indirect coupling via lattice strain or other effects may lead to anomalies in the dielectric constant $\varepsilon(T)$ in passing through the magnetic transitions. The first search for the magnetodielectric coupling detected a small anomaly of $\varepsilon$ at $T_N$ in YMnO$_3$ [7]. Similar anomalies were later found in other hexagonal manganites [1,8,9]. Very recently a correlation between the FE and AFM domain walls was shown to exist in YMnO$_3$, providing further evidence of a coupling between the two orders [10]. Similar coupling is therefore expected to exist in HoMnO$_3$ and to give rise to novel phenomena due to the complex magnetic phase diagram of the compound.

Well shaped platelike single crystals of HoMnO$_3$ of 2.5 $\times$ 2.5 mm$^2$ in size and between 50 and 300 $\mu$m thick were prepared as described elsewhere [11]. Magnetization measurements were conducted using the Magnetic Property Measurement System (Quantum Design) with the field parallel and perpendicular to the c axis. The capacitance of two crystals (70 and 240 $\mu$m thick) with gold pads sputtered onto two parallel faces was measured using the K-3330 and HP-4285A LCZ meters at frequencies between 10 kHz and 1 MHz. The Physical Property...
Measurement System (Quantum Design) was employed to control temperature and magnetic field up to 7 T.

The $c$-axis dielectric constant $\varepsilon(T)$ of HoMnO$_3$ at zero magnetic field is shown in Fig. 1. The small anomaly of $\varepsilon(T)$ at $T_N = 76$ K is in agreement with previous reports [1,8]. Additionally, a sharp peak (width $<0.6$ K, $\sim 5\%$ of the base $\varepsilon$) at 32.8 K is unambiguously detected for the first time. The peak position and its relative magnitude are independent of the measurement frequency, suggesting that the peak is related to a phase transition in the magnetic subsystem. The Mn-spin rotation transition was previously observed in HoMnO$_3$ at a $T_{\text{SR}}$ varying between 33 and 45 K, depending on the sample quality and the measurement techniques. The recent investigation of the magnetic phase diagram of single-crystalline HoMnO$_3$ [5] gives a $T_{\text{SR}} = 32.8$ K, precisely the temperature at which the $\varepsilon$ peak is observed by us. We have therefore associated the $\varepsilon$ peak with the Mn-spin-reorientation transition.

In a magnetic field $H$ parallel to the $c$ axis the $\varepsilon$ anomaly broadens and evolves into a plateau-like structure with a sharp increase at $T_1(H)$ and a quick drop at $T_2(H)$. The $\varepsilon(T)$'s at different magnetic fields are shown in Fig. 2 with their vertical axes shifted for clarity. While the overall $\varepsilon$ anomaly decreases and both $T_1$ and $T_2$ move toward lower $T$ with $H$, the $\varepsilon(T)$ outside the peak is not affected at all by $H$. The values of $\varepsilon(T)$ on both sides of the peaks are the same for all data sets and coincide with curve 5 in Fig. 2. At higher fields a second $\varepsilon$ plateau develops at lower $T$ as demonstrated by the 3.3 T data [curve 3 in Fig. 2]. With further increasing $H$ the two plateaus move toward one another and merge at 3.5 T, forming one single broad feature with a width of 15 K (curve 4 at 3.7 T). The anomaly disappears completely above 4.1 T (curve 5). All measurements were done with increasing as well as decreasing $T$ and no hysteresis was detected. The results are summarized as open circles in Fig. 3, showing $T_1$ and $T_2$ as functions of $H$. Both $T_2$ and $T_1$ exhibit reentrance and disappear at fields exceeding 3.5 and 4.1 T, respectively. They separate the novel phase ($I$ phase) from the $P_{\text{Sr}}cm$ and the $P_{\text{B}}cem$ phases. The $\varepsilon$ value of the $I$ phase, characterized by the $\varepsilon$ plateau, decreases smoothly with $T$ as $(T_c - T)^{-\alpha}$ with $\alpha = 0.01$ and $T_c = 32.8$ K (see the inset of Fig. 2). The $T_1(H)$ and $T_2(H)$ curves are similar to the phase boundary between the AFM ($B_1$) and the AFM ($B_2$) in Ref. [5] above 8 K, the present experimental limit for our dielectric measurements. The reentrant field in Ref. [5] is $\sim 3.8$ T, falling between the 3.5 and 4.1 T observed by us. This makes it difficult to assign the phase boundary in Ref. [5] to $T_1$ or $T_2$.

To verify the data of Fig. 3 and to support our conclusion about the existence of an intermediate phase, we have conducted isothermal measurements of $\varepsilon(H)$ that

![FIG. 1. Low-temperature dielectric constant of HoMnO$_3$ showing two anomalies at the onset of magnetic order ($T_N$) and the spin rotation transition ($T_{\text{SR}}$). Inset: details of the peak at $T_{\text{SR}}$.](087204-2)

![FIG. 2. $\varepsilon(T)$ for selected external magnetic fields $H$. (1) $H = 0$, (2) $H = 2.6$ T, (3) $H = 3.3$ T, (4) $H = 3.7$ T, (5) $H = 4.1$ T. Different curves are offset by a constant (indicated by dotted lines). $T_1$ and $T_2$ are marked by vertical bars next to curve 3. Inset: all data plotted on the same scale.](087204-2)
should show similar anomalies as the phase boundaries are crossed. $\epsilon(H)$ is displayed in Fig. 4 for three temperatures. Each isothermal $\epsilon(H)$ shows the expected enhancement in the $I$ phase with only one pronounced plateau like structure. The $H$ dependence of $\epsilon$ within each phase ($P6_3cm$, $I$ phase, and $P6_3cm$) is weak, as already suggested from the data of Fig. 2. The two transitions at $H_2$ (low field edge) and $H_1$ (high field edge) are included as solid circles in Fig. 3 and they are in perfect agreement with the results obtained from $\epsilon(T)$ at constant $H$. The data show no hysteresis at the transitions with increasing and decreasing $H$.

In an attempt to determine the origin of the dielectric anomaly associated with the $I$ phase, we examined the magnetic ordering of the Ho and Mn ions. An AFM order of the Ho spins along the $c$ axis was detected in neutron scattering experiments below 25 K [3], as well as below 32.5 K [2]. The details of this AFM order of the Ho spins are not yet resolved. Reference [3] suggested that only $2/3$ of the Ho moments participate in this ordering, leaving $1/3$ of Ho spins disordered with a large paramagnetic contribution to the dc susceptibility, as observed in magnetic measurements [1,3]. It is also not clear how the Ho-spin ordering is correlated with the Mn-spin rotation transition that stretches between 32.5 and 42 K in the neutron scattering studies of polycrystalline samples [2], in contrast to the results from single crystals in which the spin rotation transition is very sharp in zero field and appears close to 32.8 K [5]. Ho-spin ordering is expected to affect the $c$-axis magnetic susceptibility $\chi_c$. We have therefore conducted magnetization measurements on our HoMnO$_3$ single crystals with the external magnetic field parallel and perpendicular to the $c$ axis. Indeed, for the first time, we found a small but distinct leveling off of $\chi_c$ over a narrow temperature range ($<1$ K), as indicated by the arrow in Fig. 5 (enlarged in the lower inset). The anomaly is very sharp (as shown by $d\chi_c/dT$, upper inset of Fig. 5) and appears at exactly the same temperature (32.8 K) as the peak of $\epsilon(T)$ at zero field. When an external

![FIG. 3. Low-temperature magnetic phase diagram of HoMnO$_3$. Open circles: data from $\epsilon(T)$ scans. Solid circles: data from isothermal field scans $\epsilon(H)$. Solid stars: anomalies of the $c$-axis magnetic susceptibility. Dotted line: phase boundary according to Ref. [5].](image)

![FIG. 4. $\epsilon(H)$ for three selected temperatures. For the 26 K data the two transitions at $H_2$ and $H_1$ are indicated by vertical arrows.](image)

![FIG. 5. $c$-axis magnetic susceptibility of HoMnO$_3$. The arrow shows the anomaly associated with the AFM ordering of the Ho spins. Lower left inset: enlargement of the critical range. The derivative (upper right inset) shows a sharp peak at $T_{SR}$.](image)
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