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Large magnetodielectric effects in orthorhombic $HoMnO_3$ and $YMnO_3$

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We have found a remarkable increase (up to 60%) of the dielectric constant with the onset of magnetic order at 42 K in the metastable orthorhombic structures of $YMnO_3$ and $HoMnO_3$ that proves the existence of a strong magnetodielectric coupling in the compounds. Magnetic, dielectric, and thermodynamic properties show distinct anomalies at the onset of the incommensurate magnetic order and thermal hysteresis effects are observed around the lock-in transition temperature at which the incommensurate magnetic order locks into a temperature independent wave vector. The Mn^{3+} spins and Ho^{3+} moments both contribute to the magnetodielectric coupling. A large magnetodielectric effect was observed in $HoMnO_3$ at low temperature where the dielectric constant can be tuned by an external magnetic field resulting in a decrease of up to 8% at 7 T. By comparing data for $YMnO_3$ and $HoMnO_3$ the contributions to the coupling between the dielectric response and Mn and Ho magnetic moments are separated.

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The coupling between dielectric and magnetic properties recently observed in some manganites[1–6] and in other oxides[7,8] is of fundamental interest and of eminent significance for potential applications. The anomalies of dielectric (magnetic) properties at magnetic (ferroelectric) phase transitions and the possibility of tuning the dielectric constant (magnetization) by external magnetic (electric) fields open alternate perspectives in the basic understanding of the interesting materials and for the design of devices. The magnetodielectric effect can be explained by a spin-lattice coupling due to an increase of magnetic exchange energy when the magnetic ions shift their positions.[9,10] This effect is particularly strong close to or below a magnetic phase transition and may result in structural anomalies and a change of the dielectric properties.

The rare earth manganites, RMnO$_3$ (R=rare earth metal), exhibit strong magnetic exchange interactions between the magnetic moments of the Mn^{3+} ions as well as some of the magnetic R^{3+}. Depending on the rare earth ionic size, RMnO$_3$ crystallizes in either hexagonal or orthorhombic (distorted perovskite) structure with the structural phase boundary between Ho and Dy. However, some of the hexagonal compounds can also be synthesized as a metastable phase in the orthorhombic structure by either special chemical procedures[11] or high pressure synthesis.[12] The hexagonal phases of RMnO$_3$ show ferroelectricity below Curie temperatures between 590 and 1000 K and antiferromagnetic (AFM) transitions below 100 K with small but distinct anomalies in the dielectric constant at or below the magnetic transitions.[1–4] Since symmetry arguments do not allow a direct coupling between the Mn magnetic order and the polarization in the hexagonal structure the observed magnetodielectric coupling has to be related to secondary interactions but a microscopic explanation of these effects is not yet available. Some work has been done to investigate possible magnetodielectric effects in the orthorhombic phases of RMnO$_3$. Most notably is the recent discovery of a giant magnetoelectric effect and the onset of ferroelectricity at the incommensurate-commensurate AFM lock-in transition in $TbMnO_3$.[5] The report reveals a wealth of physical phenomena in the spin-frustrated compound with different magnetic ions and magnetoelastic as well as magnetoelectric coupling effects.

Spin frustration and incommensurate (IC) magnetic orders are typical features of orthorhombic RMnO$_3$ with an Mn-O-Mn bond angle close to 145°. They are due to a competition of ferromagnetic and AFM interactions between the Mn^{3+} ions on nearest- and next-nearest-neighbor positions mediated by the superexchange mechanism. The IC AFM order is stable below about 50 K for rare earth ions from Eu to Ho followed at lower temperatures by a transition into *A* type AFM (Eu, Gd), *E* type AFM (Ho), or an IC magnetic structure with a fixed modulation wave vector (Tb, Dy).[13] Among the possible candidates for further investigations, $YMnO_3$ and $HoMnO_3$ are of preferred interest. Both compounds exist in hexagonal and orthorhombic structures. This allows a direct comparison of their properties in different lattice symmetries. Furthermore, the ionic radii of Y^{3+} and Ho^{3+} are very close so that the structural parameters are almost identical. The Y^{3+} ion is nonmagnetic but the Ho^{3+} carries a magnetic moment. The effect of the additional magnetic species in $HoMnO_3$ can, therefore, be resolved by comparing its properties with those of $YMnO_3$. Both compounds exhibit an IC AFM transition at about 42 K (order of the Mn^{3+} spins) and a lock-in transition into a temperature independent wave vector at lower T.[14,15] $HoMnO_3$ shows another transition below 9 K that was attributed to the AFM order of the Ho^{3+} moments.[14] It is of primary interest to investigate the dielectric constant and the magnetodielectric couplings at these transitions and to compare the results with similar observations in the hexagonal RMnO$_3$.[1,2]

We have therefore focused our attention onto the dielectric properties of both compounds in the orthorhombic structure close to the magnetic phase transitions and their dependence on external magnetic fields. We have found a large magnetodielectric effect resulting in an enhancement of the

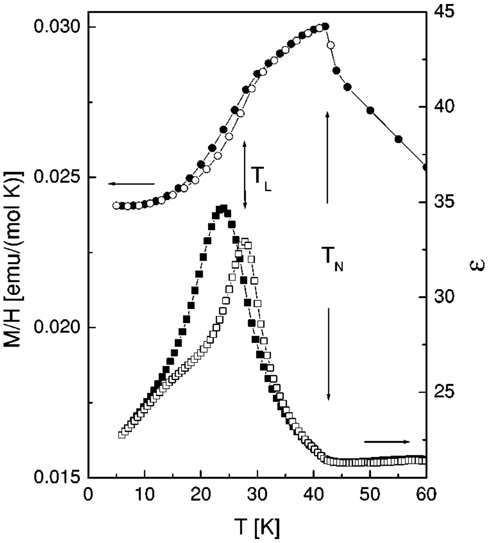

FIG. 1. Magnetization (circles, left scale) and dielectric constant (squares, right scale) as a function of temperature of orthorhombic $YMnO_3$. Closed symbols: decreasing *T*; open symbols: increasing *T*.

dielectric constant, ε, at zero magnetic field below the IC AFM transition by 60% in $YMnO_3$ and 42% in $HoMnO_3$, respectively. In $HoMnO_3$ we also show a strong dependence of ε on external magnetic fields below the lock-in transition from the IC to the commensurate magnetic order.

Single-phase hexagonal samples with nominal composition $YMnO_3$ ($HoMnO_3$) were prepared by a solid-state reaction technique. Prescribed amounts of Y_2O_3 (Ho_2O_3) and Mn_2O_3 were mixed, preheated at 900 °C (1000 °C) in O_2 for 16 h, and sintered at 1500 °C (1100 °C) for 24 hours under an oxygen atmosphere. The hexagonal compounds were transformed into the orthorhombic structure by high-pressure sintering for 5 h (1020 °C, 3.5 GPa). The phase pure *Pbnm* orthorhombic structure was obtained and no impurity phases could be detected in the x-ray spectra for both compounds. The samples were shaped for dielectric measurements into pellets about 0.5 mm thick with a contact area of 10 mm^2. The capacitance was measured between 100 kHz and 1 MHz using the HP 4285A meter and the samples were exposed to magnetic fields up to 7 T in the physical property measurement system. Magnetization measurements were conducted in fields up to 5 T employing the magnetic property measurement system.

The temperature dependence of the dielectric constant at 100 kHz is shown below 60 K for $YMnO_3$ and $HoMnO_3$ in Fig. 1 and Fig. 2, respectively. Below the IC Néel temperature, T_N, $\varepsilon(T)$ increases rapidly and passes through a maximum at lower *T*. The enhancement of ε is more than 60% in $YMnO_3$ and 42% in $HoMnO_3$. The Néel temperatures for both compounds are nearly identical, T_N=42.2 K, due to the structural similarity of both compounds. Besides the large increase of $\varepsilon(T)$ there is also a pronounced thermal hysteresis with decreasing and increasing temperatures well below T_N. Whereas T_N is exactly the same upon cooling and heating the hysteresis of $\varepsilon(T)$ is essential at temperatures below about 30 K. Therefore, it cannot be attributed to the IC Néel transition but it is rather related to the lock-in transition at which the modulation vector of the AFM order of the Mn^{3+} spins locks into a *T*-independent value.[14,15] The lock-in transition temperature, T_L, was estimated from neutron scattering data as 28 and 26 K for $YMnO_3$ and $HoMnO_3$, respectively. While the maxima of $\varepsilon(T)$ appear at lower *T* the largest slope of the increasing $\varepsilon(T)$ below T_N is close to the T_L values given above. For $YMnO_3$ the steepest increase of $\varepsilon(T)$ is at 27.5 and 29.6 K with decreasing and increasing *T*, respectively. The corresponding values for $HoMnO_3$ are 23 and 26 K. Both sets of critical temperatures are very close to the T_L's from neutron scattering. Therefore, we associate the temperatures of the steepest increase of $\varepsilon(T)$ with T_L and we conclude that the magnetic lock-in transitions show a thermal hysteresis of about 2 to 3 K that is typical for first order phase transitions. Similar hysteresis effects have also been reported in other rare earth manganites very recently.[16] The distinct anomalies in the dielectric constant and its closeness to the magnetic transitions suggest a very strong magnetodielectric coupling. In order to establish the correlation of the magnetic order and the dielectric anomalies and, in particular, the thermal hysteresis observed at T_L, we have measured the dc magnetization of $YMnO_3$ and $HoMnO_3$ between 2 and 400 K. The high temperature data show the characteristic Curie-Weiss behavior with an extrapolated paramagnetic temperature of −54 and −19 K as well as an effective magnetic moment of 5.0 and 10.8μ_B for $YMnO_3$ and $HoMnO_3$, respectively. The sets of Curie-Weiss parameters are in good agreement with previous reports.[14,15,17] The effective moments are close to the theoretical values of 4.9μ_B for $YMnO_3$ and 11.5μ_B for $HoMnO_3$. In the low temperature range the

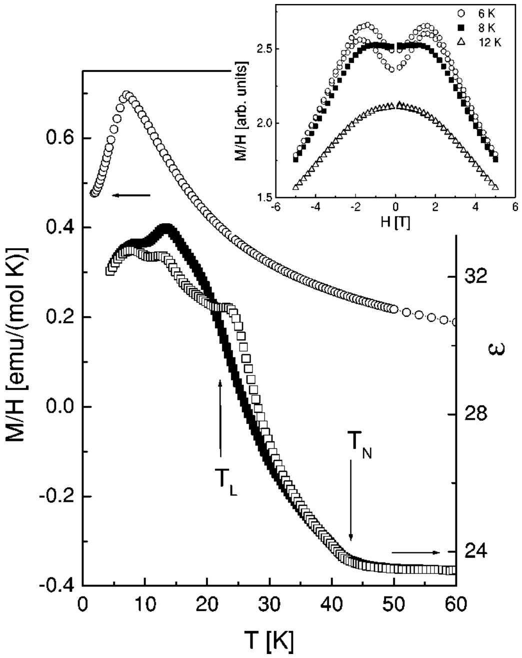

FIG. 2. Magnetization (circles, left scale) and dielectric constant (squares, right scale) as a function of temperature of orthorhombic $HoMnO_3$. Closed symbols: decreasing *T*; open symbols: increasing *T*. The inset shows the susceptibility vs field at different temperatures.

IC magnetic transition of $YMnO_3$ is clearly indicated by the maximum of the dc susceptibility (Fig. 1) at $T_N=42.2$ K which coincides with the critical temperature deduced from the upturn of $\varepsilon(T)$ discussed above. The pronounced shoulder of the susceptibility at lower T followed by a fast decrease defines the lock-in transition. The distinct hysteresis of the susceptibility close to the lock-in transition with the critical temperatures of 27.4 K upon cooling and 28.7 K upon heating has not been observed before but it is in perfect agreement with the dielectric data. The observation of the magnetic hysteresis (Fig. 1, upper curve) provides further evidence for the first order nature of this transition and unambiguously proves the coupling between magnetic order and dielectric properties. The dc magnetization of $HoMnO_3$ is dominated by the large paramagnetic moment of the Ho^{3+}. This contribution increases the magnetization of $HoMnO_3$ in the low T range by a factor of up to 20 as compared to $YMnO_3$. Therefore, anomalies at the IC spin order transition of the Mn^{3+} are barely detected in the data of Fig. 2 (upper curve). However, when the inverse susceptibility is differentiated with respect to T, a small but distinct peak appears at $T_N=42.2$ K. The major anomaly in the $HoMnO_3$ magnetization is the peak below 10 K that is due to the AFM order of the Ho^{3+} moments. Magnetic hysteresis effects as revealed in the $\varepsilon(T)$ data are barely seen in Fig. 2 since the subtle changes in the Mn^{3+} spin order at T_L are concealed by the huge contribution of the paramagnetic Ho^{3+}. Neutron scattering experiments have shown a similar hysteresis in the magnetic reflections between 10 K and 35 K in $HoMnO_3$.[17] We have measured the heat capacity, $C_p(T)$, of both compounds and observed small hysteresis effects proving the thermodynamic origin of the thermal hysteresis as seen in the dielectric and the magnetic ($YMnO_3$) data. In $HoMnO_3$ the $C_p(T)$ for cooling and heating cycles differs by up to 200 mJ/(mol K) in the temperature range between 10 and 35 K, in which also the hysteresis of $\varepsilon(T)$ was observed (Fig. 2). In $YMnO_3$ the $C_p(T)$ of the heating cycle is up to 300 mJ/mol K enhanced with respect to the cooling data between 23 and 35 K, close to the interval of magnetic hysteresis (Fig. 1). Therefore, we conclude that thermal hysteresis below T_N is an intrinsic property for both compounds and that it is related to the development of the IC magnetic order and the lock-in transition to a T-independent wavelength. The hysteresis effects on the magnetization and specific heat are very small but they appear far more pronounced in $\varepsilon(T)$. The dielectric constant is extremely sensitive to subtle changes of the magnetic order and serves as a perfect probe of the magnetic state. The IC AFM order of the Mn^{3+} is very rigid with respect to external magnetic fields. The dc susceptibilities of $YMnO_3$ measured at 1 and at 5 T, for example, are basically identical to the low-field data shown in Fig. 1 over the whole temperature range. No shift of T_N was observed with increasing H. In $HoMnO_3$, however, the magnetic order of the Ho^{3+} moments at low T is rapidly suppressed by the magnetic field.[14] The field dependence of the magnetization (Fig. 2, inset) reveals a metamagnetic transition below the Ho-ordering temperature as indicated by the maximum of M/H at $H_m=1.5$ T (6 K) and the hysteresis of M/H at low fields. The metamagnetic transition, observed also in recent measurements at low T,[12,14] disappears for $T \approx 9$ K, the transition temperature of the AFM Ho ordering.

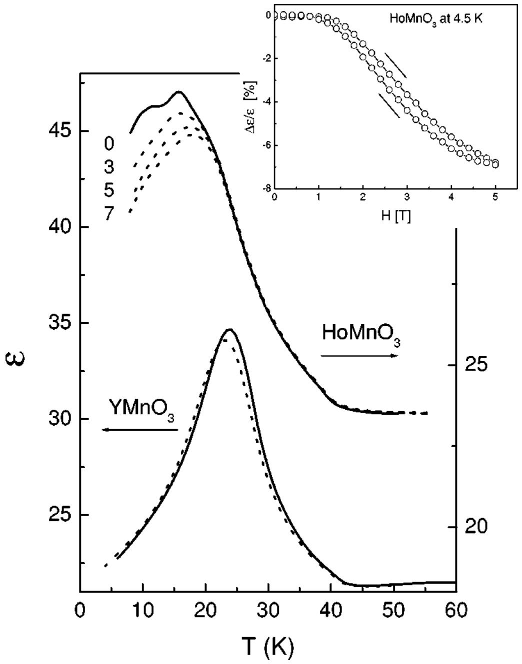

FIG. 3. Magnetodielectric effect in $YMnO_3$ (left scale, full line: $H=0$; dotted line: $H=7$ T) and in $HoMnO_3$ (right scale, full line: $H=0$; dotted lines: $H=3,5,7$ T—from top to bottom). Inset: Relative change of the dielectric constant as a function of the magnetic field for $HoMnO_3$ at 4.5 K.

The magnetic tunability of dielectric properties is of particular interest. The magnetic field dependence of the dielectric constant of $YMnO_3$ is small as shown in Fig. 3 (only cooling data are included in Fig. 3). In $HoMnO_3$, however, the external field causes a sizable decrease of $\varepsilon(T)$ in the low-T range, the magnetodielectric effect at 4.5 K is shown in the inset of Fig. 3. The dielectric constant decreases by almost 8% at 7 T. This large magnetodielectric effect provides evidence for a strong coupling of the dielectric response to the Ho^{3+} magnetic moments via magnetoelastic effects. The decrease of $\varepsilon(T)$ with H sets in below 22 K, the temperature of the lock-in transition into the E type commensurate magnetic order. The AFM order of the Ho spins below 9 K reduces the magnetic field effect on ε at low fields and $\varepsilon(H)$ is almost constant for $H<H_m$. However, $\varepsilon(H)$ decreases rapidly at fields above the metamagnetic transition as shown in the inset of Fig. 3. Neutron scattering experiments[14] have reported a small AFM magnetic moment of the Ho below 22 K that increases sharply at the main transition close to 7 K. The Ho moments lie in the (1,0,1) planes and their angle with the orthorhombic c axis increases suddenly at about 15 K and moves continuously up to 60° at $T=0$.[14] The sharp change of spin direction at 15 K is reflected in the small but distinct drop of $\varepsilon(T)$ right below its maximum temperature (Fig. 2). The magnetic field component in the (1,0,1) plane can rotate the Ho moments and, via magnetoelastic effects, change the dielectric constant. Below the AFM transition temperature (about 9 K) the Ho-spin system becomes less susceptible to the external field and the

magnetodielectric effect is small. Only when H increases above H_m do the Ho moments respond to H by rotating in the ac plane resulting in the observed decrease of $\varepsilon(H)$. We therefore conclude that the observed magnetodielectric effect in $HoMnO_3$ is a consequence of the field-induced rotation of the Ho spins in the (1,0,1) plane. It should be noted that all observations are made using polycrystalline samples and all measured quantities are averaged over the random grain orientation. It is expected that the magnetodielectric effect is even larger when well-oriented single crystals could be investigated. Unfortunately, single crystals of orthorhombic $HoMnO_3$ grown under high-pressure conditions are not yet available.

It is interesting to compare the large magnetodielectric effect observed in orthorhombic $YMnO_3$ and $HoMnO_3$ with similar dielectric anomalies in the hexagonal structures of the same compounds. The hexagonal manganites order in a frustrated AFM spin arrangement at 71 K ($YMnO_3$) and at 76 K ($HoMnO_3$). Here spin frustration is due to the geometric constraint in the triangular lattice formed by the Mn ions in the *ab* plane. In $HoMnO_3$ two additional magnetic transitions have been observed at 33 and 5 K related to Mn^{3+} spin rotation and magnetic ordering of Ho^{3+} moments. Anomalies of the dielectric constant are observed at all magnetic transitions in the hexagonal $(Y/Ho)MnO_3$, however, the magnitude of these anomalies is small.[1–3] Even the recently reported sharp peak of $\varepsilon(T)$ at the spin-rotation transition of hexagonal $HoMnO_3$, the strongest dielectric anomaly in hexagonal $RMnO_3$, does not exceed in magnitude about 4–5% of the base ε.[2] The small response in the hexagonal structures can be explained by the existing ferroelectric order that forms well above room temperature in hexagonal $YMnO_3$ and $HoMnO_3$. At the temperature of the magnetic transitions (<100 K) the electric polarization is rigid and any effects of magnetic order or magnetic fields on the dielectric constant are therefore small. The 60% increase of ε below the AFM phase of the orthorhombic structure is large and it indicates that huge magnetodielectric effects are expected in the orthorhombic rare earth manganites, as recently reported by Goto *et al.*[16]

In summary, we have demonstrated the existence of a strong coupling between dielectric properties and magnetic orders in the metastable orthorhombic structures of $YMnO_3$ and $HoMnO_3$. The dielectric constant increases by up to 60% in the IC magnetic phase below $T_N=42.2$ K. We show that thermal hysteresis exists near the lock-in transition temperature, T_L, in both compounds, typical for first order phase transitions. Both, the Mn^{3+} spins and the Ho^{3+} moments, contribute to the increase of $\varepsilon(T)$. A large magnetodielectric effect at low T in $HoMnO_3$ is explained by the magnetic field induced reorientation of the Ho moments in the *ac* plane, resulting in a metamagnetic transition below 9 K. By comparing data for $YMnO_3$ and $HoMnO_3$, the contributions to the coupling between the dielectric response and Mn and Ho magnetic moments have been separated.

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