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Strong spin-lattice coupling in multiferroic $HoMnO_3$: Thermal expansion anomalies and pressure effect

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Evidence for a strong spin-lattice coupling in multiferroic $HoMnO_3$ is derived from thermal expansion measurements along the *a* and *c* axes. The magnetoelastic effect results in sizable anomalies of the thermal expansivities at the antiferromagnetic (T_N) and the spin rotation (T_{SR}) transition temperatures as well as in a negative *c*-axis expansivity below room temperature. The coupling between magnetic orders and dielectric properties below T_N is explained by the lattice strain induced by the magnetoelastic effect. At T_{SR} various physical quantities show discontinuities that are thermodynamically consistent with a first-order phase transition.

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Among the multiferroic materials, the rare-earth manganites have attracted increasing attention because of a wealth of physical phenomena related to the coexistence of ferroelectricity with antiferromagnetic (AFM) orders. The coupling and mutual interference of ferroelectric (FE) and magnetic orders is of fundamental interest and bears the potential for future applications. For example, the orthorhombic $R\mathrm{MnO_3}$ (R=Eu to Dy) undergo several magnetic phase transitions accompanied by distinct dielectric anomalies.[1–4] Ferroelectricity and large magnetodielectric coupling have been observed in some of the compounds.[1,3]

The $R\mathrm{MnO_3}$ with smaller rare-earth ions (R from Ho to Lu, and Y) crystallize in the hexagonal $P6_3cm$ structure with ferroelectricity arising well above room temperature. The onset of AFM order of the Mn spins below 100 K gives rise to interesting physical effects related to the coupling of both orders. The first signature of the magnetodielectric effect in hexagonal manganites was discovered in $\mathrm{YMnO_3}$ as an anomaly of the dielectric constant at $T_N \approx 70$ K.[5] Similar anomalies have been subsequently reported for almost all hexagonal $R\mathrm{MnO_3}$.[6] The magnetic order of the Mn^{3+} spins is geometrically frustrated since the Mn ions form a triangular lattice in the *a*-*b* plane. Additional phase transitions at temperatures below 10 K are observed in some hexagonal $R\mathrm{MnO_3}$ with magnetic R^{3+} due to the *R*-*R* exchange correlations. Changes in the magnetic structure of the Mn spins have been reported for R=Lu, Sc, Ho at intermediate temperatures.[7] The interactions between the FE polarization, the frustrated AFM order of the Mn spins, and the *R*-ion magnetic moments give rise to a complex magnetic phase diagram as was recently revealed for example, in $\mathrm{HoMnO_3}$.[8,9] At zero magnetic field the AFM transition in $\mathrm{HoMnO_3}$ at T_N=76 K is followed by a Mn-spin-rotation transition with the onset of the AFM order of the Ho moments at T_{SR}=33 K and another magnetic transition at T_2 =5.2 K characterized by a substantial increase of the Ho sublattice magnetization combined with another rotation of Mn spins.[10] Optical[7] and neutron scattering experiments[10] have identified the magnetic symmetry of the phase between T_{SR} and T_N as $P6_3cm$ (with Mn spins perpendicular to the hexagonal *a* axis) and between T_2 and T_{SR} as $P6_3cm$ (Mn spins rotated by 90° with respect to the $P6_3cm$ phase). All three magnetic phase changes are accompanied by distinct anomalies of the dielectric constant ε, most notably a very sharp peak of ε at T_{SR} that was discovered very recently.[11]

The dielectric anomalies at the magnetic transitions of $\mathrm{HoMnO_3}$ evidence a strong correlation of the magnetic and FE orders. Whereas the direct coupling between the in-plane magnetic moments of the Mn ions and the *c*-axis FE polarization is not allowed for magnetic symmetries $P6_3cm$ and $P6_3cm$ (Ref. 12) an indirect coupling via magnetoelastic deformation and lattice strain was proposed to account for the observations.[11] No clear evidence for lattice distortions or strain has been reported so far.

We have therefore measured the thermal expansion coefficients α along the *a* and *c* axes of $\mathrm{HoMnO_3}$ over a large temperature range. We find distinct anomalies of α_a and α_c at T_N and at T_{SR} and a negative *c*-axis expansivity at all T below room temperature, revealing extraordinarily strong magnetic correlation and spin-lattice coupling effects. A sudden increase of the volume at T_{SR} suggests the first-order nature of the spin-rotation transition that is confirmed by the thermodynamic consistency of the volume, magnetization, and entropy discontinuities across the transition, as well as the pressure and magnetic field dependence of T_{SR}.

Single crystals of $\mathrm{HoMnO_3}$ have been grown from the flux[9] and by the floating zone method. The linear thermal expansivity was measured over a large temperature range below 300 K employing the strain-gauge method. Below 100 K, a high-precision capacitance dilatometer was used to resolve the thermal expansion anomalies near the magnetic phase transition temperatures, T_N and T_{SR}. The pressure dependence of T_{SR} was investigated by monitoring the sharp peak of the dielectric constant[11] for pressures up to 1.7 GPa in a Be-Cu high-pressure clamp.

The results of the dilatometric measurements of $\mathrm{HoMnO_3}$ are summarized in Fig. 1. Whereas the *a* axis behaves "normal" and shrinks with decreasing T, the *c* axis length steadily

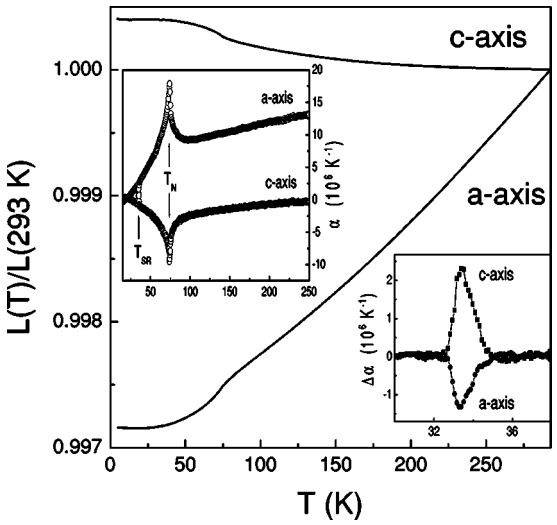

FIG. 1. Temperature dependence of the *a* and *c* axes of $HoMnO_3$ (main panel). Left inset: α_a and α_c with distinct anomalies at T_N and T_{SR}. Right inset: Anomalies of α_a and α_c at T_{SR} (the lattice contribution was subtracted).

increases from room temperature to lower *T*. This unusual behavior indicates a strong magnetic exchange and spin-lattice coupling of the Mn spins and will be discussed later. At T_N the linear expansivities α_a and α_c exhibit distinct λ-type anomalies (left inset of Fig. 1) with opposite signs. In cooling through T_N the in-plane distances are reduced and the *c* axis expands resulting in an abrupt change of slope of $a(T)$ and $c(T)$ in opposite directions. The λ shape of the peaks of α_a and α_c is typical for a second-order phase transition with a broad critical region. A similarly pronounced λ-type anomaly was also observed in the specific heat, $C_p(T)$, of $HoMnO_3$ at T_N.[9,13] The strong anomalies of α and C_p are evidence for a large magnetoelastic coupling. The Mn spins are strongly correlated via the AFM superexchange interaction in the hexagonal *a*-*b* plane. The magnetic exchange coupling along the *c* axis is much weaker. The large in-plane exchange interaction should stabilize the AFM order at a relatively high temperature. However, due to geometric frustration of the Mn spins the magnetic phase transition takes place at much lower temperature (T_N=76 K) with a special alignment of the magnetic moments so that neighboring Mn spins form an angle of 120°.[8] The small entropy change associated with the AFM transition (only 10 to 15 % of the maximum value of $R \ln 5$)[9,13] is an indication of the existence of sizable short-range correlations between the Mn spins above T_N, as derived from magnetic and neutron scattering data.[14] Strong magnetic correlations as well as long-range order are known to be a common origin of lattice strain when the magnetic energy of the system of interacting moments is lowered by a change of the interatomic distances.[15,16] In the anisotropic structure of $HoMnO_3$ the major effect of the Mn-spin exchange correlations is a reduction of the in-plane distances resulting in a magnetic contribution to the thermal expansion and an enhancement of α_a. The shortening of the *a* axis at T_N increases the force constants between the ions and provides a natural explanation for the abnormal increase of the frequency of some in-plane phonons recently observed below T_N in $HoMnO_3$.[17] The existence of strong spin-lattice coupling in hexagonal $RMnO_3$ was also concluded very recently from the observation of a large suppression of the thermal conductivity in a broad temperature range above T_N in $YMnO_3$ and $HoMnO_3$.[18]

The negative expansivity of the *c* axis below room temperature (Fig. 1) is observed for hexagonal $RMnO_3$ and its origin is yet to be explored. For anisotropic compounds it is not unusual that the thermal expansion in one crystallographic direction is negative within a limited temperature range.[19] In $HoMnO_3$, however, α_c is negative at all *T* below room temperature. Negative values of α can originate either from low-energy transverse acoustic (TA) modes of vibration, as, for example, in crystals of Si, Ga, CuCl, and others, or from magnetic interactions with strong spin-lattice coupling.[19] The soft TA modes are common in open crystal structures of low coordination number and may lead to unidirectional or isotropic negative expansivities as, for example, observed in β-$LiAlSiO_4$ and ZrW_2O_8.[20,21] However, the hexagonal rare-earth manganites do not meet the conditions of low coordination, and soft TA phonons have not been observed in the compounds. We therefore attribute the negative *c*-axis expansivity to the strong magnetic correlations and magnetoelastic coupling in the compound. The magnetic correlations of the Mn spins are strongest in the *a*-*b* plane and they increase with decreasing temperature resulting in a magnetic contribution to the in-plane thermal expansivities. At the same time, mediated by elastic forces of the lattice, the *c* axis expands with decreasing temperature, as observed in our experiments (Fig. 1). This negative expansion effect obviously dominates over the commonly positive contribution to the *c*-axis expansion that is due to the lattice anharmonicities. The volume expansivity is positive over the whole temperature range. These effects are particularly strong close to the AFM transition as reflected in the peaks of α_a and α_c at T_N (inset of Fig. 1). The opposite directions of both peaks provide further support to our conclusion. The magnetic moments of the Ho^{3+} ions order at lower temperatures (below T_{SR}) and their effect on the lattice strain between T_N and room temperature can be considered to be small.

The physical origin of the coupling between the magnetic order and dielectric properties observed in most of the hexagonal $RMnO_3$ is not yet understood.[5,6,11] In $P6_3cm$ and $P6_3cm$ symmetries the direct coupling between the in-plane staggered magnetization and the *c*-axis ferroelectric polarization is not allowed.[11,12] Therefore, the dielectric anomalies at T_N have to be a second-order effect, possibly mediated by lattice strain. Our thermal expansion measurements provide direct evidence for the existence of a sizable lattice distortion close to T_N. This distortion affects the temperature dependence of $\varepsilon(T)$ of $HoMnO_3$. The magnetodielectric effect at and below T_N was recently described by a model that includes the AFM Heisenberg exchange interaction, a double well potential for the lattice displacements giving rise to ferroelectricity, and a spin-phonon interaction term.[22] For certain values of the spin-lattice coupling constant the drop of $\varepsilon(T)$ below T_N could be qualitatively reproduced. Thereby, $\varepsilon(T)$ is a function of the inverse square of the FE displacement (along the *c* axis). To qualitatively verify this correla-

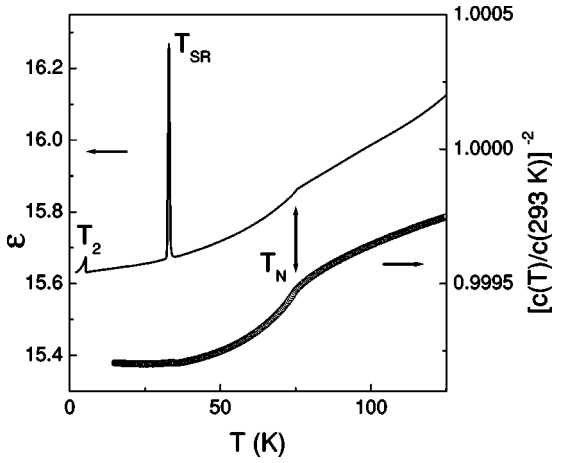

FIG. 2. Comparison of $\varepsilon(T)$ and the inverse square of $c(T)$.

tion we compare $\varepsilon(T)$ with $c(T)^{-2}$ in Fig. 2. The perfect scaling of both quantities over a broad temperature range proves unambiguously that the dielectric properties and the lattice strain induced by the magnetic correlations are intimately related.

The peak of ε at T_{SR} was shown by us to be associated with the spin-rotation transition via an intermediate phase[11] and its existence was confirmed very recently.[18] This sharp enhancement of $\varepsilon(T_{SR})$ was attributed to arise from a contribution of magnetic domain walls of domains with $P\underline{6}_3$ symmetry and the allowed linear magnetoelectric effect in the walls.[23] The steplike increase of ε at 5 K was observed before[6] and it is related to another major change of the magnetic order involving the Ho moments.[8,10] The possible magnetoelectric interactions below T_{SR} and its microscopic origin have been discussed recently including the effects of asymmetric Dzyaloshinskii-Moriya exchange interactions between Ho and Mn moments.[24] The microscopic interactions between Mn spins, Ho moments, and the FE order result in the complex phase diagram[9] and interesting physical effects such as electric field induced ferromagnetic order, etc.[24]

The spin-rotation transition is very sharp and several dielectric, magnetic, and thermodynamic quantities change abruptly at T_{SR}.[9,11] The thermal expansion measurements reveal small, but distinctive anomalies at T_{SR} resulting in sharp peaks of α_a and α_c with opposite signs (right inset of Fig. 1). Upon cooling through T_{SR} the a axis expands by $\Delta a/a = 1.52\times10^{-6}$ and the c axis shrinks by $\Delta c/c = -2.44\times10^{-6}$. This behavior is opposite to the a contraction and c expansion observed at T_N. However, it is consistent with the proposed onset of the AFM order of some Ho moments oriented along the c axis[9,10,13] and the expected c-axis contraction due to magnetostrictive effects. It is interesting to note that the volume below T_{SR} is larger than above with $\Delta V/V = -0.6\times10^{-6}$ [here $\Delta V = V(T>T_{SR}) - V(T<T_{SR})$]. The width of the spin-rotation transition as derived from anomalies of various quantities is less than 0.6 K.[9] This leads us to suggest the first-order nature of this phase transformation. At first order transitions, different thermodynamic quantities such as volume and magnetization exhibit discontinuities that contribute to the total change of entropy at the transition temperature. The entropy change at T_{SR} is given by

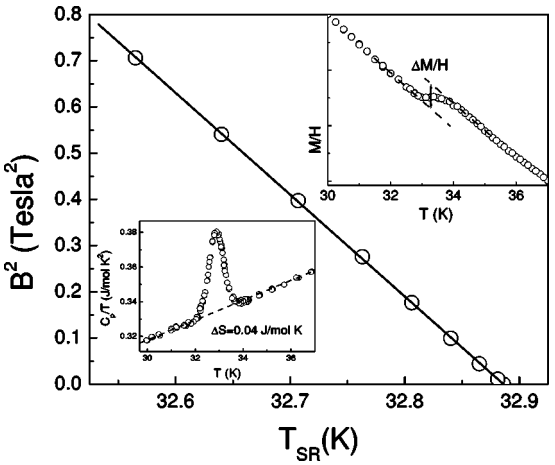

FIG. 3. Magnetic-field dependence of T_{SR} below 1 T. The right and left insets show the abrupt change of magnetic susceptibility and the heat capacity peak at T_{SR}, respectively.

$$\Delta S = \Delta V \frac{dp}{dT_{SR}} - \frac{1}{2}\frac{\Delta M}{B}\frac{d(B^2)}{dT_{SR}}. \qquad (1)$$

p, B, ΔV, and ΔM are the pressure, magnetic induction, volume discontinuity, and magnetization jump at T_{SR}, respectively. The various quantities entering Eq. (1) are experimentally accessible and will be used to prove the first-order nature of the spin-rotation transition. The phase diagram of $HoMnO_3$ shows a nonlinear decrease of T_{SR} with increasing field B.[8,9,11] For $B<1$ T we find a perfect quadratic dependence $T_{SR} \propto B^2$ (Fig. 3), with the slope $d(B^2)/dT_{SR} = -2.2\ \mathrm{T}^2/\mathrm{K}$. The jump of the magnetic susceptibility is determined from dc magnetization measurements (right inset in Fig. 3) as $\Delta M/B = 818(\mathrm{A\,m})/(\mathrm{V\,s})$. The magnetic contribution to ΔS in (1) is therefore 0.034 J/(mol K). For estimating $\Delta V dp/dT_{SR}$ the pressure dependence of T_{SR} needs to be known. We have measured the pressure shift of the sharp dielectric peak at T_{SR} in order to derive dT_{SR}/dp (Fig. 4). The peak temperature of $\varepsilon(T)$ decreases linearly with applied pressure (inset of Fig. 4) at a rate of dT_{SR}/dp

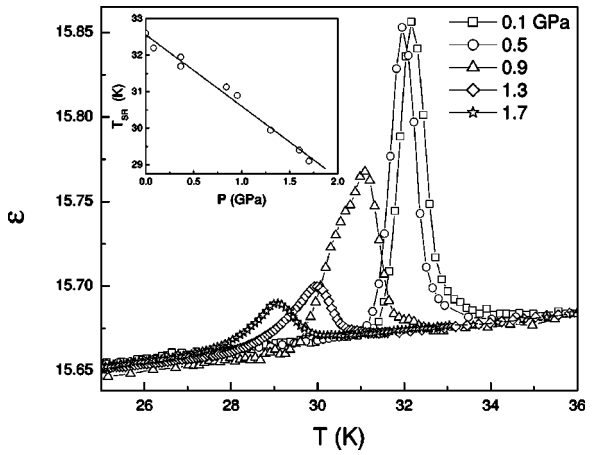

FIG. 4. Pressure effect on the peak of ε at T_{SR}. Inset: Pressure dependence of T_{SR}.

$=-2.05$ K/GPa. The decrease of T_{SR} with p is intimately related to the increase of volume right below T_{SR}. The pressure-induced compression favors the $P6_3cm$ phase (stable above T_{SR}) with the smaller volume on the expense of the $P6_3cm$ phase. From the pressure coefficient of T_{SR} and the volume change across the transition the mechanical work contribution to ΔS is estimated as $\Delta V dp/dT_{SR} = 0.01$ J/(mol K). The total entropy change according to (1) is therefore of the order of 0.044 J/(mol K). This value is to be compared with ΔS calculated by integrating the excess specific heat, C_p/T, across the phase transition. The small peak of C_p/T at T_{SR} (left inset of Fig. 3) was resolved only recently[9,18] and it corresponds to an entropy change of $\Delta S = 0.040$ J/(mol K). This value is in very good agreement with the sum of the two contributions estimated above, i.e., Eq. (1) is fulfilled within the experimental uncertainties. This shows the thermodynamic consistency of all the measured quantities (specific heat, magnetization, volume expansivity, T-H and T-p phase boundaries) and it proves the first-order nature of the spin-rotation phase transition in $HoMnO_3$. The major contribution to the entropy change is due to the change of magnetic order at T_{SR}. A detailed analysis of the c-axis magnetization above and below T_{SR} led us to suggest a partial AFM order of the Ho magnetic moments at T_{SR} and the possible existence of a correlation between the onset of the Ho order and the Mn-spin rotation.[9] The small magnetic contribution to ΔS of only 0.034 J/mol K is consistent with a small sublattice magnetization deduced from neutron scattering data[10] or a partial magnetic order at T_{SR} involving only some of the Ho moments.[13]

In summary, we demonstrated the existence of extraordinarily strong spin-spin and spin-lattice couplings over a broad temperature range in $HoMnO_3$ resulting in a sizable magnetic contribution to the a-axis thermal expansion coefficient and, via elastic coupling, in the negative c-axis expansivity below room temperature. We conclude that the dielectric anomalies observed in the hexagonal $RMnO_3$ at T_N are a consequence of this spin-lattice coupling. At the spin-rotation transition of $HoMnO_3$ various physical quantities show discontinuities indicative of a first-order phase transition. We separate the mechanical (volume expansion) and magnetic contributions to the total entropy change at T_{SR} and prove that the entropy balance required by the thermodynamics of first-order transitions is fulfilled.

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