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Giant coupling of second-harmonic generation to a multiferroic polarization

Th. Lottermoser,[1] D. Meier,[1] R. V. Pisarev,[2] and M. Fiebig[1,*]
[1]*HISKP, Universität Bonn, Nussallee 14-16, 53115 Bonn, Germany*
[2]*Ioffe Physical Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia*
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Spectroscopy reveals a giant coupling of optical second-harmonic generation to the spontaneous polarization in compounds with magnetically driven ferroelectricity. In $TbMn_2O_5$ the symmetry reduction by the ferroelectric order is detected with a sensitivity four orders of magnitude above the resolution limit of 10–100 pC/cm^2. This points to an electronic rather than ionic origin of the spontaneous polarization in joint-order-parameter multiferroics. Hence, our work constitutes an inaugural experimental statement on the controversial theoretical discussion on the nature of the multiferroic polarization.

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Cross correlations between magnetic (spin) and electric (charge) properties are a challenging topic in condensed-matter physics. An early highlight is marked by the prediction and discovery of the magnetoelectric (ME) effect, which can occur in systems with broken time- and space-inversion symmetry.[1] Later it was realized that systems with a coexistence of long-range magnetic and electric order, termed multiferroics, have a potential for displaying particularly pronounced ME effects. A refined view revealed two types of multiferroics with fundamentally different ME coupling. In *split-order-parameter multiferroics* the magnetic order breaks the time-reversal symmetry whereas the ferroelectric order breaks the spatial inversion symmetry. Because of this disjunctness the ME coupling is often weak.[2,3] In *joint-order-parameter multiferroics* magnetic ordering breaks both the spatial and the temporal inversion symmetry. Thus, a spontaneous polarization P_{sp} becomes symmetry allowed and represents a degree of freedom for minimizing the ground-state energy. The resulting ferroelectricity is magnetically induced so that the ME coupling can be extraordinarily strong, including electric domain reversal or even electric phase transitions driven by magnetic fields (or vice versa). Early examples for joint-order-parameter multiferroics are Cr_2BeO_4,[4] $TbMnO_3$,[5] and $TbMn_2O_5$.[6] A common feature of this class of multiferroics is the small value of P_{sp} of typically 1–10 nC/cm^2 as compared to $\gtrsim 10$ $\mu C/cm^2$ in many established ferroelectrics.

The microscopic origin of the magnetically driven spontaneous polarization is the topic of an intense and controversial debate. The "ionic polarization" model views the magnetostrictive displacement of ions from their centrosymmetric positions as the primary source of P_{sp}.[7–9] This resembles the conventional ionic ferroelectricity with off-center movement of the cation with respect to the anion lattice as, e.g., in $BaTiO_3$. According to the "electronic polarization" model, magnetic ordering induces P_{sp} because of the related hybridization and displacement of the electron clouds.[10,11] Notably, the electronic polarization does not require any noncentrosymmetric displacement of the nuclei. Material-wise, present theories mostly focus on orthorhombic $RMnO_3$ and RMn_2O_5. Some support a predominantly ionic[7,12] or predominantly electronic[10,13,14] ferroelectricity while others consider comparable influence of the two.[15–17] Here, experimental verification is highly desirable but hampered by the smallness of P_{sp}. Expected *ionic* displacements are in the order of 10^{-3} Å and were searched for by neutron, x-ray, and Raman experiments, again with contradictory results.[12,18–24] Attempts to evidence an *electronic* contribution to P_{sp} may have not been made at all. The existence of magnetically induced ferroelectricity of electronic origin in joint-order-parameter multiferroics thus remains an open question.

In this Rapid Communication, electronic contributions to the spontaneous polarization in $TbMn_2O_5$ are revealed by optical second-harmonic generation (SHG). Three independent contributions to the net polarization are uniquely identified and separated by SHG spectroscopy. Giant coupling to the SHG process allows us to detect the symmetry reduction imposed by the ferroelectric order with a sensitivity of 10–100 pC/cm^2. Comparison to other compounds reveals that an electronic polarization seems to be a general feature of multiferroics with magnetically induced ferroelectricity.

SHG describes the induction of a light wave at frequency 2ω by a light wave at frequency ω.[25,26] The component χ_{ijk} of the corresponding nonlinear susceptibility tensor couples j and k polarized contributions of the incident light field to an i polarized contribution of the SHG light field. In the electric-dipole approximation $\hat{\chi}$ is a polar tensor with $\hat{\chi} \neq 0$ in noncentrosymmetric systems only.[25] Thus, SHG is well suited for detecting ferroelectricity that breaks the inversion symmetry[27] because contrary to linear optical techniques the ferroelectric SHG contribution emerges background free. Microscopically, SHG originates in optically driven transitions between electronic states. Because of this electronic nature SHG is particularly sensitive to electronic (in comparison to ionic) contributions to ferroelectricity. This sensitivity will be further enhanced if transitions involving the $3d$ band are probed, whose electrons are responsible for the magnetic order and any acentric redistributions of the electron density following from it.

The joint-order-parameter multiferroic investigated here is $TbMn_2O_5$. Crystals are orthorhombic at room temperature (point symmetry *mmm*) with crystallographic axes related to the Cartesian coordinate system of our experiment via $a=x$, $b=y$, and $c=z$. Incommensurate antiferromagnetic Mn^{3+} and Mn^{4+} ordering described by the propagation vector $(k_x,0,k_z)$ with $k_x \approx \frac{1}{2}$ and $0<k_z<\frac{1}{4}$ occurs at $T_0=43$ K. At $T_1=38$ K

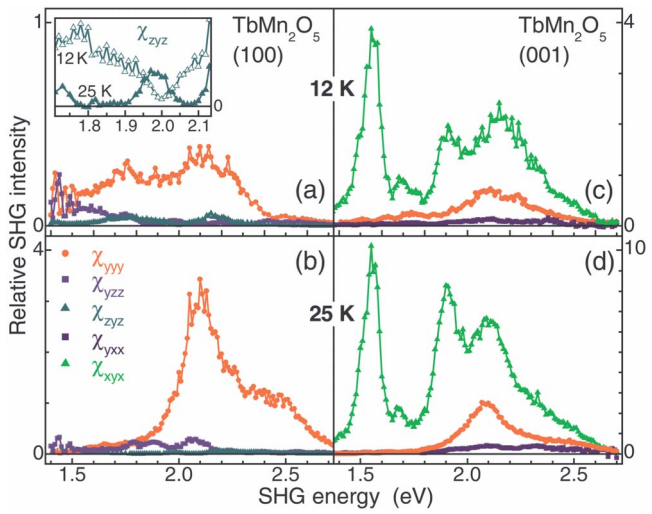

FIG. 1. (Color online) SHG spectra of multiferroic $TbMn_2O_5$ for all nonlinear susceptibilities $\chi_{ijk} \neq 0$ in the commensurate and the incommensurate multiferroic phase at 25 and 12 K, respectively. The spectra for the (100) and (001) crystals are shown while (010) crystals do not display a detectable SHG signal. The same scale is used for SHG intensities in (a)–(d).

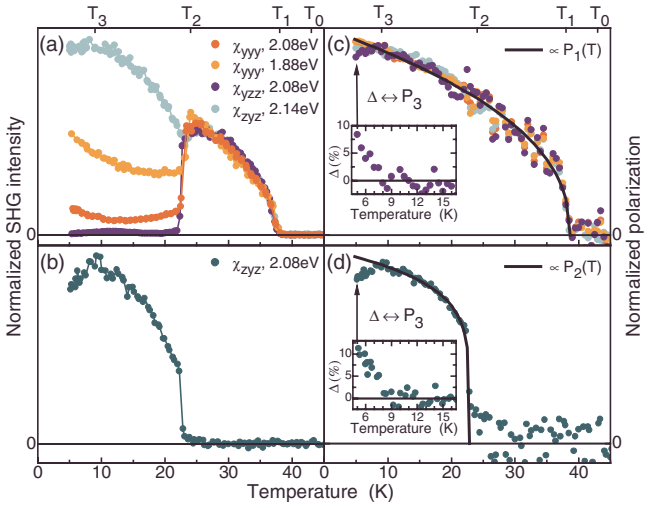

FIG. 2. (Color online) Temperature-dependent SHG intensity and spontaneous polarization in $TbMn_2O_5$. (a) SHG intensity for various photon energies and polarizations. (b) SHG intensity for χ_{zyz} at 2.08 eV. (c) and (d) Contributions to the spontaneous polarization P_{sp}. The parametrization of P_{sp} in terms of P_{1-3} was derived from (a) and (b) and is critically discussed in the text. Straight lines are derived from fits of $I_{SHG} \propto (1 - T/T_{1,2})^{\beta}$. Insets show the deviation Δ between fits and data indicating the presence of a third contribution P_3 to the spontaneous polarization.

a two-stage lock-in to a commensurate antiferromagnetic state with $\vec{k}=(\frac{1}{2},0,\frac{1}{4})$ and a spontaneous polarization along the b axis sets in. At $T_2=24$ K the antiferromagnetic order becomes incommensurate again and P_{sp} changes drastically. At $T_3 \approx 9$ K long-range Tb ordering is assumed to occur.[28] Because of the temperature and magnetic-field dependence of P_{sp} it was proposed that P_{sp} is composed of two contributions.[6] In a detailed treatment of all magnetic phases of $TbMn_2O_5$ by Landau theory[29] it was shown that on the basis of symmetry a polarization $P_1 \propto \rho_1 \rho_2$ below T_1 is complemented by a contribution $P_2 \propto \rho_1 \rho_3$ below T_2 to form the net polarization $P_{sp}=P_1+P_2$ with ρ_{1-3} as order parameters. However, experimental confirmation of the composite nature is still due because the pyrocurrent measurements applied thus far reveal the net polarization only.

In our experiment, polished flux-grown (100), (010), and (001) oriented $TbMn_2O_5$ single crystals with a lateral extension of a few mm and a thickness of ~ 50 μm were mounted in a liquid-helium-operated cryostat accessing the temperature range of 5–325 K. SHG was measured in transmission in the spectral range from 1.7–2.7 eV using an experimental setup described elsewhere.[26]

Figure 1 shows SHG spectra gained on (100) and (001) oriented $TbMn_2O_5$ crystals in the commensurate (25 K) and the incommensurate (12 K) multiferroic phase whereas no SHG was detected in the range $T_1 < T < T_0$. A pronounced spectral dependence is observed for all the SHG contributions in Fig. 1. The transitions correspond to the lowest $O \rightarrow Mn$ charge-transfer excitations.[30] Only the tensor components χ_{ijk} depicted in Fig. 1 contribute to SHG. In particular, no SHG was observed with a (010) oriented $TbMn_2O_5$ sample. Tensor components with a different ijk set reveal a different spectral dependence except for the degeneracy $\chi_{ijk}=\chi_{ikj}$.[25] Hence, the set of independent tensor components contributing to SHG includes χ_{yyy}, χ_{yzz}, χ_{zyz}, χ_{yxx}, and χ_{xyx}, i.e., all possible ijk triplets with two different indices and an odd number of y polarized contributions. This is exactly the set of polar tensor components allowed for the crystallographic point symmetry $m2m$.[26] Remarkably, $m2m$ is the symmetry obtained from an orthorhombic crystal (point symmetry mmm) after developing a spontaneous polarization along its y axis. We thus conclude that SHG in Fig. 1 detects the reduction of symmetry by the spontaneous polarization. However, the signal evidencing this is not at the limit of detection[12,18–24] but 4 orders of magnitude above this threshold.

Comparison of the data in Fig. 1 taken at 25 and at 12 K reveals changes in the amplitude and, more surprisingly, a spectral redistribution of the SHG signal when going through the phase transition at T_2. Note that at $T > T_2$ the SHG intensity for χ_{zyz} is zero in the range from 1.77–1.91 and 2.06–2.09 eV while below T_2 a SHG signal is observed. Apparently, there are at least two independent contributions to the spontaneous polarization: one at $T < T_2$ detected in this spectral range and one at $T > T_2$ that is not. Because of this selectivity separation of different contributions to P_{sp} should be possible by SHG spectroscopy. This is exploited in Figs. 2(a) and 2(b) which show the temperature dependence of the SHG intensity I_{SHG} at different polarizations and photon energies. The universal temperature dependence at $T > T_2$ in Fig. 2(a) indicates that a single contribution $I_{SHG} \propto |a_1(2\omega)P_1(T)|^2$ to the spontaneous polarization, with a_1 as coupling coefficient, constitutes the SHG signal in this range.

Below T_2 the temperature dependence to the SHG signal is not universal anymore. This is only possible if at least two contributions to the spontaneous polarization with $I_{SHG} \propto |a_1(2\omega)P_1(T)+a_2(2\omega)P_2(T)|^2$ are present. As revealed

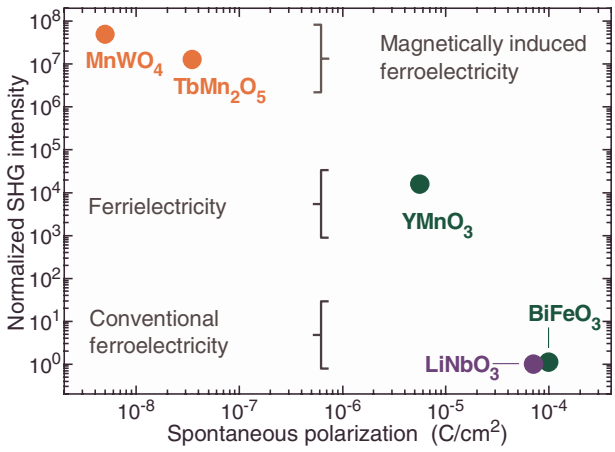

FIG. 3. (Color online) Normalized SHG yield for various joint- and split-order-parameter multiferroics and a model ferroelectric. Data points were derived as detailed in the text.

by Fig. 1 the spectral dependence of a_1 and a_2 is different which explains the nonuniversal temperature dependence below T_2 in Fig. 2. This is most strikingly expressed by Fig. 2(b) where $a_1=0$ and $a_2\neq 0$. Figure 2(b) can be employed for separating P_1 from P_2 (and any additional contributions) in Fig. 2(a) by fitting the complex coefficient a_2 such that P_1 and $\partial P_1/\partial T$ continue steadily through T_2.[6,29] This leads to the temperature dependence of P_1 and P_2 shown in Figs. 2(c) and 2(d), respectively. The universality of these data sets shows that no other contributions than P_1 and P_2 are present in $TbMn_2O_5$ above T_3. However, below T_3 the data begin to diverge and to deviate from the power law fitted to them. This indicates the presence of a third, yet unclaimed contribution to the net polarization emerging at T_3. It is related to the long-range order of the Tb spins at this temperature. The insets in Figs. 2(c) and 2(d) reveal $T_3=(9.3\pm 0.9)$ K.

Hence, SHG allows us to uniquely identify and separate three independent contributions to the spontaneous polarization of multiferroic $TbMn_2O_5$ emerging at three different temperatures. In the past, the emergence of the third contribution P_3 was considered possible but not explicitly discussed. Note that P_{1-3} are separated entirely on the basis of symmetry and spectroscopy which does not allow one to identify the microscopic origin of P_{sp}. Thus, the different contributions might nevertheless be associated to the same site in the unit cell.[29]

Figure 3 shows normalized SHG intensities obtained from various types of spontaneously polarized materials. $TbMn_2O_5$ and $MnWO_4$ are both joint-order-parameter multiferroics with magnetically induced ferroelectricity. They were chosen as model end compounds with respect to their very different microscopy. $MnWO_4$ is a non-rare-earth compound with $Mn^{2+}(S=5/2)$ in which multiferroicity is driven exclusively by antisymmetric spin-spin interactions whereas $TbMn_2O_5$ is a rare-earth compound with $Mn^{4+}(S=3/2)$ and $Mn^{3+}(S=2)$ in which symmetric spin-spin interactions participate in driving the multiferroic state.[7,13,31] The two compounds are contrasted to three ionic ferroelectrics which are model compounds for ferroelectricity driven by electrostatic effects ($YMnO_3$), by electronic lone pairs ($BiFeO_3$), and by hybridization ($LiNbO_3$), respectively. In addition, $YMnO_3$ (Refs. 3 and 32) and $BiFeO_3$ (Ref. 33) are split-order-parameter multiferroics while $LiNbO_3$ is a textbook ferroelectric without accompanying magnetic order. Normalized SHG intensities are obtained by calculating $I_{SHG}^{norm}=I_{SHG}/(P_{max}^2\cdot d)$ and plotting its maximum value in the range from 1.2–3.2 eV. Here P_{max} is the maximum value of the spontaneous polarization and d is the depth of the sample up to which a contribution to the net SHG yield occurs. The value of d is determined by absorption and phase matching.[25] Thus, I_{SHG}^{norm} represents the efficiency of the coupling between the spontaneous polarization and the SHG yield.

The joint-order-parameter multiferroics display a "giant" SHG yield which is three to seven orders of magnitude higher than for the ionic ferroelectrics shown in Fig. 3. The huge difference strongly points to an electronic nature of the spontaneous polarization of these compounds. In the split-order multiferroics $YMnO_3$ and $BiFeO_3$ and also in the ferroelectric-only compound $LiNbO_3$ the polarization is obtained through nuclear movements by geometric, lone-pair, or displacive effects.[32,34] However, the coupling of the nuclear displacements to the light field is small because it is based on secondary shifts of the electron cloud induced by the nuclear displacement. In contrast, the coupling of the light field to a primary noncentrosymmetric redistribution of the electron cloud is orders of magnitude more efficient. As mentioned, the SHG process probes the electrons and, in particular, those electronic transitions involved in the magnetic and the magnetically induced ferroelectric order. Thus, the small value of the spontaneous polarization in the electronic ferroelectrics is compensated by the giant efficiency of the SHG process so that spontaneous polarizations down to $10-100\ \mathrm{pC/cm^2}$ can be detected.

It is remarkable that irrespective of the aforementioned very different microscopy and composition of the spontaneous polarization in $TbMn_2O_5$ and $MnWO_4$ their normalized SHG yield is very similar. With all the aforementioned differences between the two compounds this is a strong hint that the electronic polarization is common to joint-order-parameter multiferroics in general. Apparently, electronic contributions to the spontaneous polarization occur whenever breaking of the inversion symmetry by magnetic order induces ferroelectricity. Because of the huge difference of I_{SHG}^{norm} for electronic versus ionic contributions to the polarization SHG acts as a projector that extracts the former while suppressing the latter which can be useful for verifying theories predicting a mixture of the two.[15–17]

The placement of the split-order-parameter multiferroics in Fig. 3 is noteworthy. $BiFeO_3$ is an incommensurate spin-spiral multiferroic like $MnWO_4$ and, in part, $TbMn_2O_5$. However, ferroelectricity is caused by nuclear displacement with lone-electron-pair formation and occurs independent of the magnetic order. This clearly places the compound among the ionic ferroelectrics in Fig. 3. $YMnO_3$ yields the largest value of I_{SHG}^{norm} among the ionic ferroelectrics. Its spontaneous polarization is $5.6\ \mu\mathrm{C/cm^2}$ but composed of partly compensating sublattice polarizations that are larger.[32] Maximum SHG yield as in Fig. 3 is expected in spectral regions where, just as in Fig. 2(b) and the inset in Fig. 1(a), SHG is sensitive to one of the sublattices only. In such case SHG reproduces a

higher polarization than the net value of 5.6 $\mu C/cm^2$. This requires renormalization of the data point of $YMnO_3$ to lower values and enhances the separation between SHG from electronic and ionic contributions to the spontaneous polarization.

In summary, we observed a giant coupling of optical SHG to the spontaneous polarization in compounds with magnetically driven ferroelectricity such as $TbMn_2O_5$. Comparative measurements indicate that the giant coupling occurs independent of the microscopy and composition. Normalized SHG yields are up to seven orders of magnitude larger than in multiferroics in which magnetic and electric order occur independently. The same discrepancy holds in comparison to conventional ferroelectrics. The extraordinary sensitivity of SHG to spontaneous polarizations as low as 10–100 pC/cm^2 allowed us to uniquely identify and separate three independent contributions to the net ferroelectric polarization in $TbMn_2O_5$. The giant coupling is associated to an electronic rather than ionic origin of the spontaneous polarization because SHG probes the electronic system directly and, hence, with much higher efficiency than for nuclear displacements affecting the SHG yield in an indirect way only. Our work thus represents an inaugural experimental statement on the ongoing and controversial theoretical discussion on the nature of the multiferroic polarization.

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*fiebig@hiskp.uni-bonn.de

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