$k = 0$ Magnetic Structure and Absence of Ferroelectricity in SmFeO$_3$

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SmFeO$_3$ has attracted considerable attention very recently due to its reported multiferroic properties above room temperature. We have performed powder and single crystal neutron diffraction as well as complementary polarization dependent soft X-ray absorption spectroscopy measurements on floating-zone grown SmFeO$_3$ single crystals in order to determine its magnetic structure. We found a $k = 0$ G-type collinear antiferromagnetic structure that is not compatible with inverse Dzyaloshinskii-Moriya interaction driven ferroelectricity. While the structural data reveal a clear sign for magneto-elastic coupling at the Néel-temperature of $\sim$675 K, the dielectric measurements remain silent as far as ferroelectricity is concerned.

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The discovery of magnetism induced ferroelectricity has renewed interest in multiferroic materials due to the enhanced magnetoelectric interaction in these materials that makes them very interesting for technical applications [1,2]. Recently, it has been found that ferroelectricity can arise from some special types of magnetic structures inducing sizeable magnetoelectric effects and the ability to switch the electric polarization by an applied magnetic field (and vice versa). In these recently studied materials, magnetic frustration induces a complex magnetic structure with cycloids or spirals [1]. However, also the ordering temperatures need to be above room temperature in order to make these materials interesting for technical applications.

Very recently, the discovery of ferroelectric polarization in SmFeO$_3$ has been reported below $T_N \sim 670$ K. The origin of this ferroelectric polarization is highly debated [3–5]. A further spin-reorientation transition occurs at $T_{SR} \sim 480$ K in this material without having any noticeable effect on the ferroelectric polarization. In the initial publication an inverse Dzyaloshinskii-Moriya interaction based mechanism has been reported to be the driving force of the ferroelectric properties of SmFeO$_3$ [3]. The underlying $k = 0$ magnetic structure was not directly measured but calculated by $ab$ initio calculations [3]. However, it has been demonstrated that this calculated $k = 0$ magnetic structure with magnetic ions located at inversion centers cannot be responsible for a spin-orbit-coupling driven ferroelectric polarization by $\mathbf{S}_i \times \mathbf{S}_j$ in this material since inversion symmetry will not be broken [4]. Within this context, an alternative mechanism based on $J\mathbf{S}_i \cdot \mathbf{S}_j$ exchange-striction has been proposed to be responsible for the ferroelectric polarization in SmFeO$_3$ [5].

Here, we report the experimentally observed magnetic structure of SmFeO$_3$ and reanalyze the ferroelectric properties of SmFeO$_3$. A large reddish SmFeO$_3$ single crystal with $T_N \sim 675$ K has been grown at a Crystal Systems Corp. 4-mirror optical floating zone furnace. The high sample quality of this insulating reddish orange single crystal has been confirmed by EDX, Laue, and x-ray diffraction techniques as well as by magnetization and Mössbauer spectroscopy measurements; see the Supplemental Materials [6]. In the inset of Fig. 1(a) a polarization microscope image is shown that indicates—together with our Laue diffraction analysis—that our SmFeO$_3$ crystals are single domain single crystals. No impurity phases are visible in highly accurate synchrotron radiation powder x-ray diffraction measurements that have been performed at beamline B2 of DORIS-III at DESY. The lattice parameters, unit cell volume and relative expansion of the lattice parameters of SmFeO$_3$ ($Pbnm$ setting with $a < b < c$) are shown in Figs. 1(a), 1(b). The $b$-lattice parameter exhibits a small anomalous kink around $T_N$ that is indicative for magnetoelastic coupling at the magnetic ordering temperature $T_N$. The other lattice parameters exhibit much less pronounced anomalies at $T_N$ that are even only barely visible in the derivatives of the lattice parameters; see Figs. 1(c), 1(d).

The highly neutron absorbing properties of the element Sm ($\sim$5900 barn for 2200 m/s neutrons) hampered the...
Here, we present two complementary neutron measurements where we were able to overcome these obstacles and measure the magnetic structure of SmFeO$_3$ directly. First, we have performed powder neutron diffraction measurements at comparably low neutron energies ($\lambda = 1.8857$ Å) with a special sample geometry at the HRPT diffractometer (SINQ). We were able to overcome the highly neutron absorbing properties of Sm by filling the outer volume of a hollow vanadium cylinder with a special mixture of fine SmFeO$_3$ powder that we “diluted” with fine aluminum powder in order to suppress the Sm absorption effects. As can be seen in Fig. 2, we obtained qualitatively good powder neutron diffraction patterns at 300, 515, and 720 K that could be easily refined with two additional phases of Al and V which do not interfere at all with the SmFeO$_3$ magnetic signal and barely interfere with structural contributions. Therefore, a reliable Rietveld refinement of the magnetic structure of SmFeO$_3$ could be performed.

Since we measured only at temperatures above room temperature, we neglected any Sm ordering [8]. As pointed out in great detail in Ref. [4], there are four different irreducible representations $\Gamma_1^+$, $\Gamma_2^+$, $\Gamma_3^+$, and $\Gamma_4^+$ corresponding to the following four spin configurations for the Fe ordering: $A_xG_yC_z$, $G_xA_yF_z$, $F_xC_yG_z$, and $C_xF_yA_z$, which correspond to the magnetic space groups $Pbnm$, $Pbn'$, and $Pbn'm'$, respectively [9]. Our neutron measurements at 300, 515, and 720 K clearly show that there appears $F_xC_yG_z$-type and $G_xA_yF_z$-type antiferromagnetic ordering in SmFeO$_3$ at 300 and 515 K, respectively. The Rietveld fits of the magnetic intensities are shown in Fig. 2 and the corresponding magnetic moments are listed in Table I in the Supplemental Material [6]. Other spin configurations or incommensurate magnetic structures can be excluded for SmFeO$_3$. We have also performed complementary single crystal neutron diffraction measurements. By choosing an optimized small sample geometry and high incident neutron energies we were able to perform single crystal neutron diffraction measurements at the D9 diffractometer (ILL). The temperature dependence of some prominent magnetic intensities are shown in Fig. 3(a).
Finally, we were able to determine the magnetic structure of SmFeO₃. We have measured the polarization dependent Fe-L edge x-ray absorption spectra (XAS) at the NSRRC in Taiwan. The spectra were recorded with the 08B beam line of the National Synchrotron Radiation Research Center (NSRRC). The calculated spectra are listed in Ref. [15]. The corresponding FeO₆ cluster considered in our calculations is also shown in the right part of each figure. One can see that the experimental spectra are nicely reproduced by the calculated spectra with spins parallel to c axis at 440 and 490 K, respectively, thus, corroborating the collinear magnetic structure obtained in our neutron measurements. 

Also our Fe-L₂,₃ edge x-ray magnetic circular dichroism (XMCD) spectra as well as our Mössbauer spectroscopy measurements are fully consistent with the fact that there is only one Fe³⁺ species in SmFeO₃; see the Supplemental Material [6].

Finally, we measured the anisotropic dielectric properties of single crystalline thin plates of SmFeO₃. The capacitance was measured over a range of frequencies with an excitation...
The dielectric loss, \(\tan \delta\), becomes slightly conductive at high temperatures (several k\(\text{K}\)) and increases. All samples are insulators at room temperature and at 800 K. No apparent anomalies could be observed in the dielectric constant \(\varepsilon\) with electric field along the \(b\) axis, \(\varepsilon_b\), (b) The tangent loss \(\tan \delta\). (c) The \(C-V\) curve of SmFeO\(_3\) at room temperature with the corresponding loss data in the inset.

FIG. 5 (color online). Dielectric characterization of SmFeO\(_3\) with the electric field along the \(b\) axis at different testing frequencies. (a) The temperature-dependent dielectric constant \(\varepsilon_b\). The hysteresis loop reported to occur at 300 K in Ref. [3] may then be attributed to leakage currents [16] which is absent in our experiment. Perhaps this is related to the different lossy character of flux-grown [3] and floating zone grown single crystals. The absence of ferroelectric properties in SmFeO\(_3\) is also consistent with the \(k = 0\) magnetic structure that we observed. This has to be contrasted with the case of other isostructural multiferroic materials, like TbMnO\(_3\), where non-collinear chiral magnetic structures have been observed [17]. We note that for a \(G\)-type antiferromagnetic rare-earth orthoferrite \(RFeO_3\), the electric polarization induced by exchange striction is known to occur only below the rare earth magnetic ordering temperature which is two orders of magnitude lower than \(T_N\) [18]. If exchange striction would be an important mechanism in SmFeO\(_3\) one would expect to see also a pyrocurrent signal when the magnetic structure exhibits distinct changes at \(T_{SR}\) which is not experimentally observed [3]. Finally, we would like to remark that magnetoelastic effects are not only present in prototypical multiferroic materials like BiFeO\(_3\) [19,20] but (across the doping series Bi\(_{1-x}\)La\(_x\)FeO\(_3\) [21]) also in non-ferroelectric centrosymmetric materials like LaFeO\(_3\) [22,23]. Our findings suggest that magnetoelastic effects may also lead to an artificial observation of pyrocurrents and, hence, magnetoelastic coupling can easily be mis-interpreted as a ferroelectric response.

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\[\varepsilon_b(\omega) = \frac{\varepsilon_2 \omega^2}{\Omega^2 + \omega^2}\]
[15] FeO$_6$ cluster parameters [eV]: $U_{dd} = 5.0$, $U_{pd} = 6.0$, $\Delta = 3.0$, $10D q = 1.2$, $\Delta e_g = 0.04$, $\Delta t_{2g} = 0.02$, $D u = -0.015$, $E_g^{\text{Mix}} = 0.02$, $pd\sigma = -1.4$, and $pd\pi = 0.64$, Slater integrals 75% of Hartree-Fock values.