Absence of Ferroelectricity in $SmFeO_3$

This report features the work of Chang-Yang Kou, Zhiwei Hu, Liu-Hao Tjeng and their co-workers published in Phys. Rev. Lett. ***113****, 217203 (2014).*

Ferroelectric polarization in $SmFeO_3$ has been recently reported below $T_N \sim 670$ K, but the origin of this polarization is highly debated.[1-3] In addition, it has been pointed out that a spin-reorientation transition occurs at $T_{SR} \sim 480$ K in this material has no noticeable effect on its polarization. Initially, a mechanism based on an inverse Dzyaloshinskii-Moriya interaction was proposed as the driving force of the ferroelectric properties of $SmFeO_3$.[1] However, the underlying $k = 0$ magnetic structure was not directly measured, but was inferred from electronic structure calculations.[1] This calculated $k = 0$ structure with magnetic ions located at inversion centers has been argued not to be responsible for the ferroelectric polarization by $S_i \times S_j$ driven spin-orbit-coupling as inversion symmetry is broken.[2] Subsequently, an alternative mechanism based on $JS_i \cdot S_j$ exchange-striction was proposed to be responsible for the ferroelectric polarization in $SmFeO_3$.[3]

In the present work, overcoming the highly neutron-absorbing properties of Sm in neutron measurements, Chang-Yang Kou, Zhiwei Hu, Liu-Ho Tjeng and their co-workers observed antiferromagnetic ordering of types $F_XC_YG_Z$ and $G_XA_YF_Z$ in $SmFeO_3$ at 300 and 515 K, respectively. As pointed out in Ref. 2 for $SmFeO_3$ (with magnetic ions located at inversion centers), $k = 0$ magnetic structures are incompatible with an electric polarization induced by an inverse Dzyaloshinskii-Moriya interaction.

The antiferromagnetic properties of $SmFeO_3$ were further studied with Fe-$L_{2,3}$ edge Xray absorption spectra dependent on linear polarization at 440 and 490 K with the Poynting vector of the light being parallel to axes *a*, *b* and *c*, shown in Figs. 1(a)–1(c). The experimental data were recorded at TLS beamline 08B1. They observed considerable X-Ray Magnetic Linear Dichroism (XMLD) signals between electric field $E \parallel b$ and $E \parallel c$ in Fig. 1(a), between $E \parallel a$ and $E \parallel c$ in Fig. 1(b), but nearly no difference between $E \parallel a$ and $E \parallel b$ in Fig. 1(c). The sign of the XMLD signals is reversed from 440 K to 490 K; see Figs. 1(a)–(b). This effect is similar to previous work on the Morin transition of hematite,[4] revealing a rotation of the spin

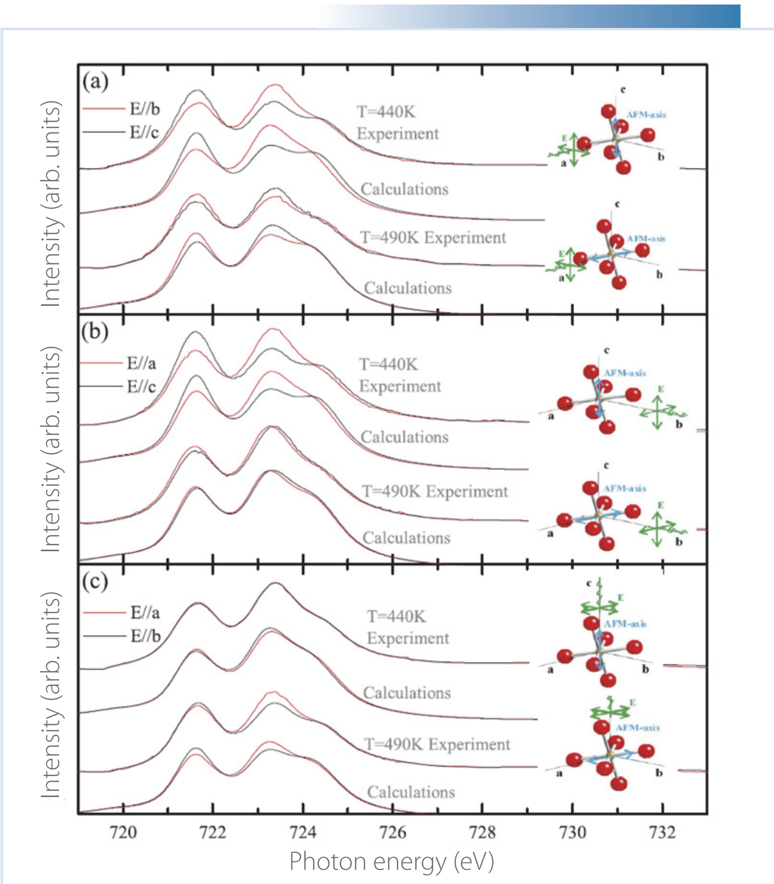

Fig. 1: Fe $L_{2,3}$ Xray absorption spectra of $SmFeO_3$. (a)–(c) XAS dependent on linear polarization measured above and below T_{SR} with the incident beam parallel to axes *a*, *b* and *c*.

orientation across T_{SR} in $SmFeO_3$. To extract the orientations of the antiferromagnetic axes, the authors simulated the spectra with configuration-interaction cluster calculations.[5] The calculated spectra are shown in Figs. 1(a)–1(c); the parameters used in their calculation are listed in Ref. 6. The corresponding FeO_6 cluster considered in their calculations is shown in the right part of each figure. The experimental spectra are evidently reproduced with the calculated spectra with spins parallel to axes *c* and *a* at 440 and 490 K, respectively, thus corroborating the collinear magnetic structure obtained in their neutron measurements.

In seeking ferroelectrity, they measured the anisotropic dielectric properties of single-crystalline thin plates of $SmFeO_3$. The capacitance was measured for frequencies over a range with an excitation level 1 V, while the temperature was swept at a small rate of warming or cooling (1–2 K/min). As shown in Figs. 2(a)–2(b), the temperature-dependent relative permittivity with electric field along axis *b*, $\varepsilon_b(T)$ shows only a broad hump with strong frequency dependence below ~ 600 K. The dielectric loss, tan δ, increased rapidly with increasing temperature. All samples are insulators near 300 K and become slightly conductive at high temperatures (several kΩ at 800 K). No apparent anomalies were observed in $\varepsilon_b(T)$ about T_N. If an intrinsic ferroelectric transition had occurred at T_N, the corresponding anomalies should be observable in both ε_b and tan δ, irrespective of testing frequencies. Also, $\varepsilon_b(T)$ and $\varepsilon_{bc}(T)$ exhibit no anomalies at T_N. Complementary measurements of capacitance and voltage (C-V) were made on all their samples at 295 K.

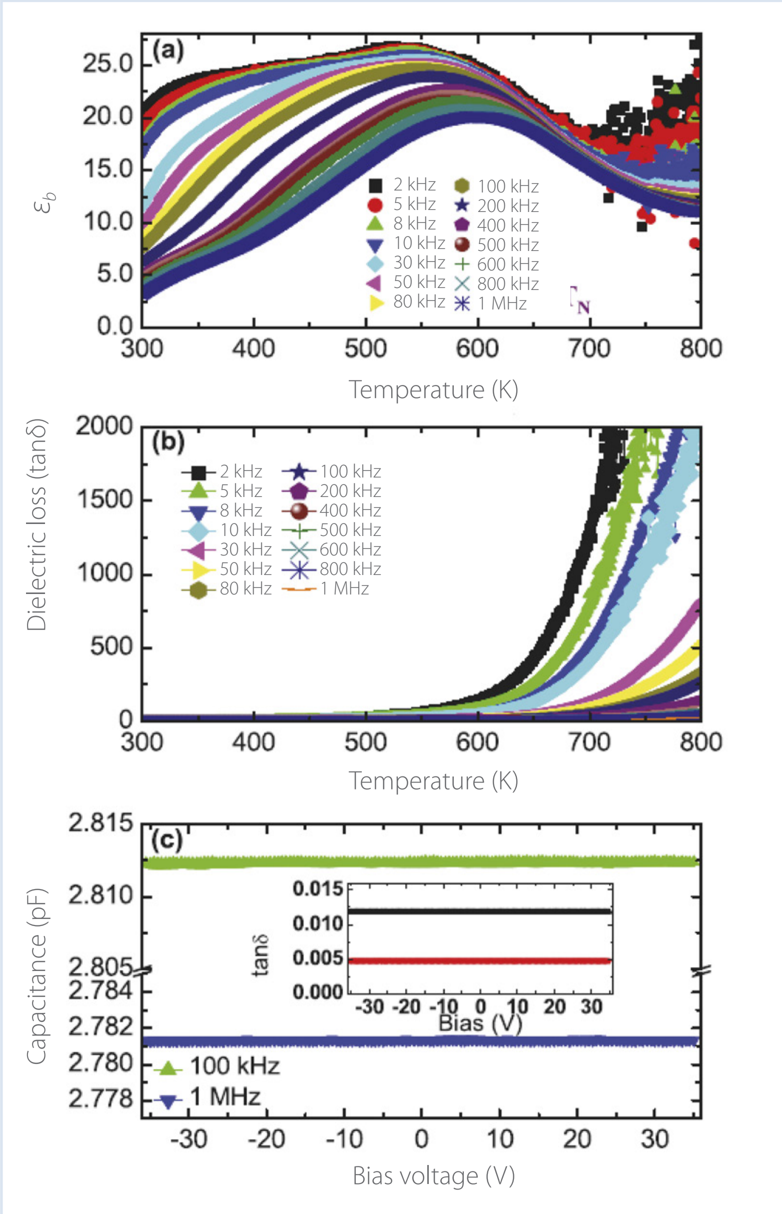

Fig. 2: Dielectric characterization of $SmFeO_3$ with electric field along axis *b* at varied testing frequency. (a) Relative permittivity dependent on temperature, ε_b. (b) Tangent loss tan δ. (c) C-V curve of $SmFeO_3$ at 295 K with the corresponding loss data in the inset.

Figure 2(c) shows a typical C-V curve with the electric field applied along axis *b*. No hysteresis was observed for $SmFeO_3$ within the experimental resolution (< 10^{-4}). It hence excludes the existence of ferroelectricity in $SmFeO_3$.

Interpreting the observations differently from the authors of Ref. 1, they suggest that strain might be induced by magnetoeleastic coupling at T_N that would be responsible for an artificial observation of a pyrocurrent in direction *b* at T_N. Their measurements of powder X-ray diffraction with synchrotron radiation reveal anomalies of predominantly the *b*-lattice parameter of $SmFeO_3$ at T_N.

The hysteresis loop reported to occur at 300 K in Ref. 1 might then be attributed to a leakage current[7] that is absent from their experiment. This effect is perhaps related to the disparate lossy character of flux-grown[1] and floating-zone-grown single crystals. The absence of ferroelectric properties in $SmFeO_3$ is also consistent with the $k = 0$ magnetic structure that they observed.

For a G-type antiferromagnetic rare-earth orthoferrite $RFeO_3$ (R = rare earth), the electric polarization induced by exchange striction is known to occur only below the rare-earth magnetic ordering temperature, which is about 0.01 times T_N. If exchange striction were an important mechanism in $SmFeO_3$, one would expect also a pyrocurrent signal when the magnetic structure exhibits distinct changes at T_{SR}, which is not experimentally observed.[1] They remark that magnetoelastic effects are present not only in prototypical multiferroic materials such as $BiFeO_3$ but (across the doping series $Bi_{1-x}La_xFeO_3$) also in non-ferroelectric centrosymmetric materials such as $LaFeO_3$. Their findings indicate that magnetoelastic effects might also lead to an artificial observation of pyrocurrents; magnetoelastic coupling can hence be easily misinterpreted as a ferroelectric response. (Reported by Hong-Ji Lin)

References

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