Comment on "Spin-Canting-Induced Improper Ferroelectricity and Spontaneous Magnetization Reversal in $SmFeO_3$"

It was reported that $SmFeO_3$ develops an improper ferroelectric polarization below 670 K, induced by noncollinear G-type antiferromagnetic order determined through *ab initio* calculations [1]. We demonstrate by group theoretical analysis that the proposed magnetic structures are incompatible with the observed electric polarization. For comparison, we include an analysis of the isostructural compound $DyFeO_3$ [2]. All irreducible representations (irreps) are labeled according to the convention of Miller and Love [3].

The paramagnetic phase of $SmFeO_3$ has space group $Pbnm$. The reported $k = 0$ magnetic structure below T_N had moment directions $S_1 = 3.55\hat{x} + 0.02\hat{y} - 0.04\hat{z}$, $S_2 = -3.55\hat{x} - 0.02\hat{y} - 0.02\hat{z}$, $S_3 = 3.55\hat{x} - 0.02\hat{y} - 0.04\hat{z}$, and $S_4 = -3.55\hat{x} + 0.02\hat{y} - 0.02\hat{z}$, where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit vectors coincident with the orthorhombic basis, and S_1 to S_4 label the Fe sites as in Ref. [1].

Eight one-dimensional irreps are associated with the little group. All eight, and the four parity-even, irreps enter into the magnetic representation of the Sm and Fe sites, respectively. The irreps and associated spin configurations are given in Table I. Contrary to that reported [1], the above magnetic structure cannot be described by a single irrep. This is manifest in the different $\hat{z}$ components of $S_1(S_3)$ and $S_2(S_4)$. The structure is described by $\alpha_i\Gamma_2^+ + \beta_i\Gamma_3^+$, where α_i and β_i are coefficients in the linear sum of the basis vectors parallel to $i = x$, y, and z, which take the values $\alpha_x = 3.55$, $\alpha_y = 0$, $\alpha_z = 0.03$, $\beta_x = 0$, $\beta_y = 0.02$, and $\beta_z = -0.01$. Mixing the two point symmetries ($m'm'm$ and $mm'm'$) breaks both m_x and m_z, giving the nonpolar point group $2'/m'$, which does not support an electric polarization.

At $T_r^{Fe} = 480$ K, $SmFeO_3$ undergoes a spin reorientation transition to $F_xC_yG_z$ (Γ_3^+) [1]. A single irrep structure was reported for this phase (labeled Γ_2 [1]); however, the point symmetry is $mm'm'$, which is also nonpolar. Furthermore, $S_1(S_4)$ and $S_2(S_3)$ were assigned separate magnetic orbits [1]. The separate orbits intrinsically require the n-glide to be broken, which contradicts the reported single irrep magnetic structure.

In $DyFeO_3$, the iron sublattice orders at $T_N^{Fe} = 645$ K with structure $G_xA_yF_z$ [2], described by the single irrep, Γ_2^+, and nonpolar point symmetry $m'm'm$. A spin reorientation transition occurs at $T_r^{Fe} = 37$ K to the $A_xG_yC_z$ structure [2], which is described by the single irrep Γ_1^+ with point symmetry mmm, also nonpolar. At $T_N^{Dy} = 4$ K, the dysprosium sublattice orders with G_xA_y, while the iron sublattice remains unchanged [2]. The Dy and Fe magnetic sublattices are described by Γ_1^- and Γ_1^+, respectively. The point symmetry of the two irreps differ by time-reversal symmetry, breaking the m_x, m_y, and m_z symmetry elements, giving the nonpolar point group 222. A metamagnetic transition occurs at $H_r^{Fe} = 24$ kOe $\| c$ axis, which induces a ferromagnetic component on the Fe sublattice $\| c$ axis. This transition returns the Fe magnetic structure to $G_xA_yF_z$ [2]. The Dy and Fe sublattices are now associated with Γ_1^- and Γ_2^+, respectively. The m_z symmetry element is broken and the phase adopts the *polar* point group $m'm'2$, allowing $\boldsymbol{P} \| c$.

TABLE I. Spin configurations in Bertaut's notation [4].

Irrep	Fe sites	RE sites	Point symmetry
Γ_1^+	$A_xG_yC_z$	C_z	mmm
Γ_2^+	$G_xA_yF_z$	F_z	$m'm'm$
Γ_3^+	$F_xC_yG_z$	F_xC_y	$mm'm'$
Γ_4^+	$C_xF_yA_z$	C_xF_y	$m'mm'$
Γ_1^-	⋯	G_xA_y	$m'm'm'$
Γ_2^-	⋯	A_xG_y	mmm'
Γ_3^-	⋯	A_z	$m'mm$
Γ_4^-	⋯	G_z	$mm'm$

To conclude, the analysis of $DyFeO_3$ is in agreement with experimental results [2]. However, in $SmFeO_3$ it is clear that the proposed magnetic structures cannot give rise to the observed electric polarization. In general, a $k = 0$ magnetic structure with magnetic ions located at inversion centers cannot, for any arbitrary spin configuration, break inversion symmetry and induce an electric polarization. Further studies of the magnetic structure are required to determine the origin of the reported polarization.

R. D. Johnson,[1,2,*] N. Terada,[1,2,3] and P. G. Radaelli[1]
[1]Clarendon Laboratory
Department of Physics
University of Oxford
Oxford, OX1 3PU, United Kingdom
[2]ISIS Facility
Rutherford Appleton Laboratory-STFC
Chilton, Didcot, OX11 0QX, United Kingdom
[3]National Institute for Materials Science
Sengen 1-2-1, Tsukuba, Ibaraki, 305-0047, Japan

Received 10 October 2011; published 21 May 2012
DOI: 10.1103/PhysRevLett.108.219701
PACS numbers: 75.50.Ee, 71.15.Mb, 77.65.−j, 77.84.−s

*r.johnson1@physics.ox.ac.uk

[1] J.-H. Lee, Y. K. Jeong, J. H. Park, M.-A. Oak, H. M. Jang, J. Y. Son, and J. F. Scott, Phys. Rev. Lett. **107**, 117201 (2011).
[2] Y. Tokunaga, S. Iguchi, T. Arima, and Y. Tokura, Phys. Rev. Lett. **101**, 097205 (2008).
[3] S. C. Miller and W. F. Love, *Tables of Irreducible Representations of Space Groups and Co-Representations of Magnetic Space Groups* (Pruett, Boulder, 1967).
[4] E. F. Bertaut, *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. 3, p. 149.

 © 2012 American Physical Society