Polar atomic displacements in multiferroics observed via anomalous x-ray diffraction

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The minute polar atomic displacements in multiferroics are shown to be within the reach of crystallography. A nonconventional methodology with anomalous x-ray diffraction is employed to investigate such displacements in $DyMn_2O_5$ with giant magnetoelectric coupling and two distinct Mn^{3+} and Mn^{4+} sites. Intensity differences of a selected Bragg reflection were measured as the direction of electric polarization is switched by a poling field. A significant differential effect, which is strongly enhanced at energies near and above the Mn K edge, was observed near and below the ferroelectric transition temperature, $T_c \sim 40$ K. The direct participation of ionic displacements in the ferroelectric polarization, particularly the Mn^{3+} sublattice, is demonstrated, dismissing a purely electronic mechanism for the multiferroicity.

For the so-called improper ferroelectrics (FEs), electric polarization is not the main order parameter, rather appearing as a by-product of some other ordering. In particular, the magnetism-driven ferroelectrics (or type-II multiferroics) have attracted great attention since the coupling between electrical and magnetic order parameters offers the possibility of controlling electrical properties with magnetic fields and vice versa (for reviews, see Refs. [1–5]). The current increase in interest in the field of multiferroics began with the discovery of strong couplings between electric polarization and dielectric constant with magnetic fields in the rare-earth manganese oxides $Tb(Dy)MnO_3$ and $Tb(Dy)Mn_2O_5$.[6–8] Significant progress in the understanding of the underlying mechanisms of magnetoelectric couplings was obtained by detailed studies of complex magnetic structures of these and other multiferroics.[9–14] Nonetheless, the expected atomic displacements in these magnetism-driven ferroelectrics are very small, lying in the scale of 10^{-3} Å or smaller.[15–18] Standard crystallographic measurement methods, however, have not been successful to unambiguously determine the symmetry and atomic displacements of the polar crystal structures. For example, a noncentrosymmetric structure (space group $Pb2_1m$) has been suggested for the ferroelectric phase of the RMn_2O_5 family (R=Y, rare earth),[15] in contrast to the paraelectric (PE) centrosymmetric structure with $Pbam$ space group, while x-ray diffraction (XRD) and neutron-diffraction studies have not unambiguously resolved the low-symmetry structure, to the best of our knowledge. It has been a matter of concern that such minute displacements might be outside the practical limits of crystallography, preventing the development of a complete physical picture for multiferroicity.

The atomic scattering factors of light may be written as $f=f_0+\Delta f'+i\Delta f''$, where $\Delta f'$ and $\Delta f''$ are the dispersion corrections. Above atomic absorption edges, the imaginary term $\Delta f''$ become appreciable, and the so-called Friedel pairs [(hkl) and $(\overline{hkl})$ reflections] show unequal intensities for noncentrosymmetric structures. This is indeed a classical crys-

tallographic method to demonstrate the lack of inversion center in a given crystal. However, in reflection geometry of x-ray diffraction, usually employed for inorganic single crystals, Friedel pairs are only accessed through different surfaces [Fig. 1(a)] and a precise evaluation of small intensity differences of Friedel pairs is not generally attainable.

In this work, a nonconventional approach to observe Friedel pairs in ferroelectric materials is employed. We demonstrate that minor polar atomic displacements may be observed by x-ray diffraction. The main difficulties found in standard Friedel pair measurements in ferroelectrics, such as physical rotation of the sample and the presence of ferroelectric domains, can be overcome by our approach. The crystal is oriented and cut in a thin-flat plate geometry, with the surface normal being parallel to the ferroelectric polarization. A poling electric field is applied and Bragg peak intensities are collected for both field polarities, switching the direction of the polar atomic displacements. As shown in Fig. 1(c), the resulting difference of Bragg intensities is analogous to the Friedel pair measurements [Fig. 1(a)]. The pseudo-Friedel pair differences [PFPDs, i.e., I^+-I^- in Fig. 1(c)] may be collected with great precision, limited solely by the photon beam and the mechanical stability at the sample position. Such precision, allied to the removal or induction of an uneven population of ferroelectric domains by the external field, is a key to reach the necessary sensitivity to probe the minute polar atomic displacements in magnetism-driven ferroelectrics. The employed methodology shows similarities to the well-known modulation technique used to investigate field-induced atomic displacements in piezoelectric materials,[19–31] except for the fact that switching dc fields are applied here.

A single crystal of $DyMn_2O_5$ was grown by the flux method as described in Ref. 6 and a thin slab was cut along the (0 1 0) plane with a thickness of ~ 0.25 mm. The sample was mounted in a closed-cycle cryostat using a special sample holder as illustrated in Fig. 1(d). A dc voltage of ± 900 V was applied between the cooper base and a thin x-ray transparent Al foil, that was located slightly above the
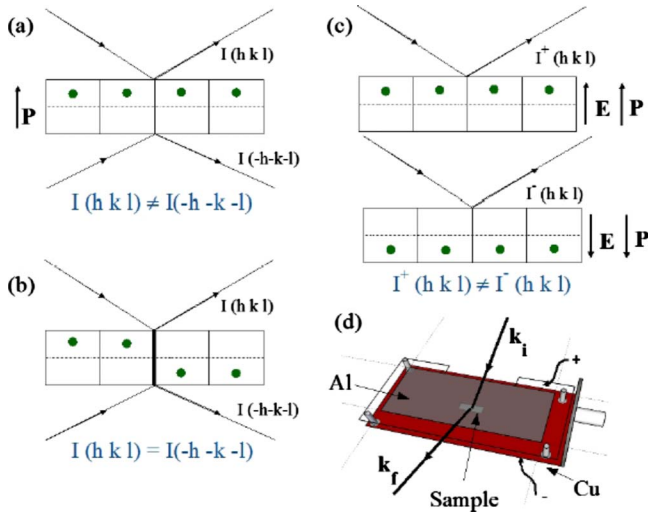
FIG. 1. (Color online) Pictorial description of the method employed in this work, where a unit cell of a ferroelectric material is represented by a square with an off-centered atom for simplicity. (a) Conventional Friedel pair data collection, in which the Bragg intensities $I(hkl)$ and $I(\overline{hkl})$ are measured using x-ray energies slightly above an absorption edge of interest, where the imaginary dispersion correction to the corresponding atomic scattering factor is non-null. For noncentrosymmetric structures, $I(hkl) \neq I(\overline{hkl})$. (b) In the more realistic case with the presence of ferroelectric domains with equal populations, the Friedel pair differences vanish. (c) With application of an external electric field, the ferroelectric domains are unbalanced or removed, and the electric polarization P and the corresponding polar atomic displacements may be reversed. Measurement of $I(hkl)$ for both field polarities (I^+ and I^-) is equivalent to the Friedel pair measurement displayed in (a). (d) Scheme of the sample holder attached to the cold finger of a closed-cycle cryostat (see text).

FIG. 2. (Color online) Detection of the PFPD. (a) An axial (θ-2θ) scan is performed for the chosen (3 6 2) reflection with applied fields along opposite polarities [I^+ and I^-, see Fig. 1(c)]. (b) The PFPD, $I^+ - I^-$, is obtained as the filled area for a given energy. Observed (symbols) and simulated (line) energy dependencies of the (c) integrated intensity and (d) PFPD of the (3 6 2) reflection through the Mn K edge, corrected by the absorption coefficient μ. The vertical dashed line indicates the chosen condition for the subsequent measurements at fixed energy.

sample surface. A thin polyester film was used to isolate the Al foil from the sample and holder. This setup does not allow for a precise determination of the actual electric field within the sample although it is simple and appropriate for the proof-of-principle measurements shown in this work. X-ray diffraction data were taken under reflection geometry on the XRD-2 beamline of the Brazilian Synchrotron Laboratory (LNLS). The intensities I^+ and I^- for the selected Bragg reflection were obtained by cycling the dc-voltage polarities in the sequence +, −, −, +, +, −, −, +. No differences between the intensities obtained with the same field polarity were observed. Therefore, the average intensity was then taken for each polarity. Temperature-dependent experiments were performed on warming after cooling the sample down to 12 K at zero field.

Figure 2(a) shows an axial (θ-2θ) scan through the (3 6 2) Bragg reflection of $DyMn_2O_5$ for x-ray energy of 6.550 keV at $T = 28$ K in electric fields with both polarities along the **b** axis. This reflection was chosen because preliminary simulations indicated that the relative magnitude of the PFPD signal with respect to the reflection intensity would be particularly large, therefore, easily and unambiguously observed. In fact, a significant PFPD signal, as large as ∼6% of the total intensity, was observed for this reflection [see Fig. 2(b)]. Due

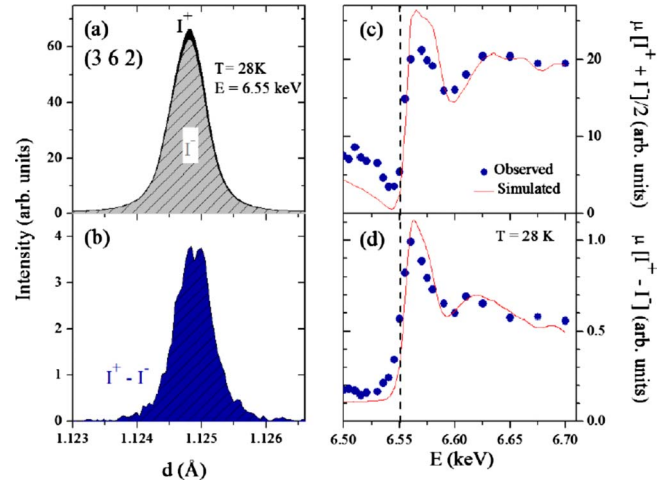to the dispersive correction of the Mn atomic scattering factor, the reflection intensity show a strong energy dependence near the Mn K edge with a nearly complete accidental cancellation near 6.550 keV [see Fig. 2(c)]. The energy dependence of the PFPD is distinct and shows a large enhancement above the edge with a significant signal at ∼6.550 keV, therefore, this condition [dashed vertical line in Figs. 2(c) and 2(d)] was chosen for the subsequent measurements at fixed energy. An estimation of the expected energy dependence of the peak intensity and PFPD was performed, using deviations from the paraelectric structure (Ref. 32) according to the ferroelectric $Pb2_1m$ space group[15,16] [solid lines in Figs. 2(c) and 2(d)]. For these simulations, the imaginary component of the Mn atomic scattering factor $\Delta f''(E)$ were extracted from fluorescence emission data through the Mn K edge for corrections for self-absorption effects. The real part of the dispersion correction $\Delta f'(E)$ was obtained from $\Delta f''(E)$ using the Kramers-Kronig relations. Tabulated values were used for the dispersion corrections of the Dy and O atomic scattering factors[33] since the employed x-ray energies were far from the corresponding absorption edges. The energy dependence of the observed intensity and PFPD are in good agreement with simulated results. We should note that no magnetic contribution is allowed for integer (hkl) reflections, considering the magnetic propagation vector $k \sim [0.49, 0, 0.25]$ for $DyMn_2O_5$ (Refs. 9, 12, 34, and 35) and, therefore, only the electronic charge sector are being probed by these measurements. Since modifications of structure factors due to the polarization of electronic density in the ferroelectric phase are expected to be negligibly small,[19,36] it is clear that the observed PFPD is associated with poling atomic displacements, dismissing a purely electronic mechanism for ferroelectricity in these materials.
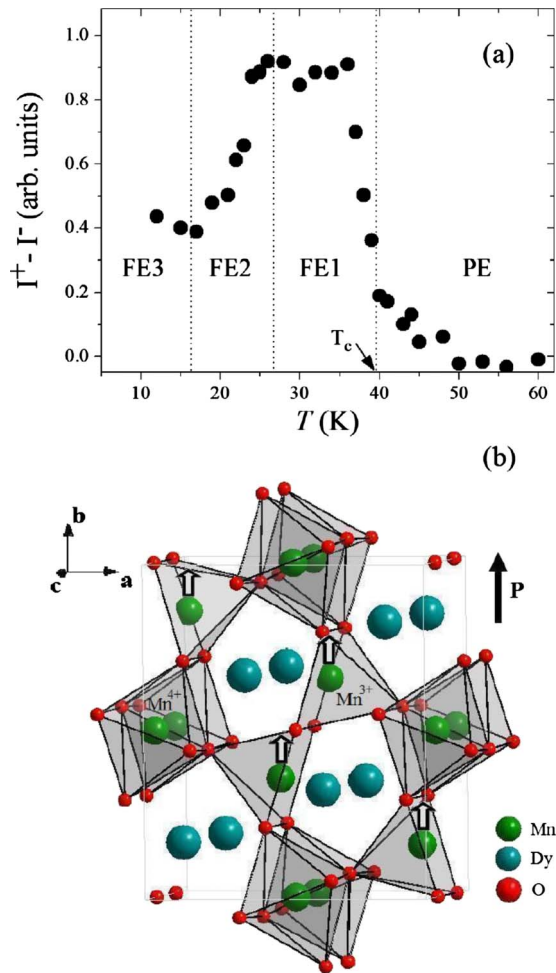
FIG. 3. (Color online) (a) Temperature dependence of the PFPD of the (3 6 2) reflection, $I^{+}-I^{-}$. The vertical dashed lines mark the transitions from the PE state to a ferroelectric state (FE1) at $T_c \sim 40$ K and between distinct ferroelectric states (FE2 and FE3) at ~ 27 and ~ 14 K, respectively, such as reported in Refs. 37 and 38. (b) Representation of the crystal structure of $DyMn_2O_5$, showing the polar displacements of the Mn^{3+} ions along the **b** axis captured by the PFPD of the (3 6 2) reflection. The direction of the polar atomic displacements and the polarization P can be switched by an external field [see also Fig. 1(c)].

From our data at the Mn K edge, it is clear that polar displacements of Mn ions play a determinant role in the ferroelectricity of $DyMn_2O_5$. Two distinct Mn ions are present [see Fig. 3(b)] in the fairly complex crystal structure of this compound,[32] where Mn^{4+} ions are found in the center of oxygen octahedra, while Mn^{3+} ions are surrounded by square pyramids. Since our technique is diffraction based, site specific information about the polar displacements may be obtained. Of course, details of the polar atomic displacements associated with the FE states cannot be unambiguously determined before a large set of PFPD data is extracted for several reflections, which is beyond the scope of this proof-of-principle study. Nonetheless, some relevant information can be still obtained with this single reflection. In fact, the PFPD of the (3 6 2) reflection was simulated considering independent displacements of Mn^{3+} and Mn^{4+} ions along the ferroelectric polarization direction (**b** axis). It was found that the PFPD signal is strongly sensitive to Mn^{3+} and completely insensitive to Mn^{4+} polar displacements along **b** against an otherwise rigid structure. Thus, our observation of a significant PFPD signal for this reflection (Fig. 2) provides direct experimental support to the predictions that the ferroelectric polarization in this family is largely generated by polar displacements of the Mn^{3+} ions [see Fig. 3(b)].[9,12,15,16]

Figure 3(a) shows the temperature dependence of the PFPD at the (3 6 2) reflection. This signal shows a rich evolution below $T_c \sim 40$ K, which seems to be correlated with the transitions to different ferroelectric states (FE1, FE2, and FE3) observed by previous specific-heat, electric, and thermal-expansion measurements.[37,38] In addition, the transition between FE2 and FE3 appears to be related to a transition between two distinct ordered magnetic states at ~ 18 K,[9,12,34,35] while the transition between FE1 and FE2 is not related to any obvious change in magnetic structure reported so far. Since ferroelectricity in this compound is believed to be magnetically driven, the FE1/FE2 transition is intriguing. It is interesting to note that the macroscopic ferroelectric polarization is larger for FE2 than for FE1,[37] while the PFPD signal is stronger for FE1 [Fig. 3(a)]. This indicates that such transition is not merely due to a change in the overall amplitude of atomic displacements, but rather involves more complex atomic and/or electronic rearrangements. It is worth mentioning that the PFPD of the (3 6 2) reflection does not vanish immediately above T_c. This is possibly due to antiferromagnetic correlations slightly above T_c, as reported in other studies,[39–41] which might led to a incipient ferroelectric state. Above ~ 50 K, no PFPD signal is observed, indicating that field-induced atomic displacements[19–31] are negligible in comparison to the polar displacements in the FE state.

In conclusion, our results provide a clear route toward a crystallographic method aimed at systematically solving the polar atomic displacements in weak ferroelectrics such as the magnetism-driven multiferroics. The (3 6 2) reflection of $DyMn_2O_5$ at the Mn K edge provides a large PFPD effect with respect to the reflection intensity, which was particularly convenient for this proof-of-principle experiment. Detection of the PFPD of several Bragg peaks will allow for unambiguous quantitative site- and element-specific determination of the minute polar atomic displacements in these materials. The joint knowledge of both the ferroelectric and the corresponding magnetic structures with element specificity,[35,42–46] that can now be envisaged, will certainly lead to a deeper understanding of the mechanisms of magnetoelectrical coupling in these materials.

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