DAFS Measurements near Pb L_{III} Edge in $Pb(Nb_{2/3}Mg_{1/3})O_3$ Single Crystal

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Introduction

$Pb(Nb_{2/3}Mg_{1/3})O_3$ (PMN) is a relaxor ferroelectric whose unusual physical properties are believed to be related to the competition of different types of atomic displacements correlated on the short-range scale. We found that several types of superlattice reflections exist in PMN. One of them is associated with the chemical ordering of Nb and Mg ions. However, it was also suggested that correlated on the short-range scale Pb displacements and oxygen octahedra rotations also contribute to the structure factor of these superlattice reflections [1, 2]. In this work, we employed the diffraction anomalous fine structure (DAFS) scattering technique near the Pb L_{III} absorption edge in order to expose any possible contributions of correlated Pb displacements.

Methods and Materials

Measurements were performed on undulator beamline 33-ID at the University-National Laboratory-Industry Collaborative Access Team (UNI-CAT) sector. The single crystal of $Pb(Nb_{2/3}Mg_{1/3})O_3$ ferroelectric relaxor used for these measurements had the shape of a platelet with linear dimensions of $2\times 4\times 1$ mm^2. The two largest parallel surfaces were sputtered by gold to produce transparent electrical contacts for *in situ* application of a dc electric field (up to 4 kV/cm). The crystal was positioned in the closed-loop He flow cryostat (Displex) with an operational temperature range of 10–300K. The cryostat was mounted on a Newport single-crystal kappa diffractometer. A graphite analyzer with a mosaic spread of ~0.4° was used for diffuse scattering measurements. The analyzer crystal was positioned on the 2θ arm of the diffractometer at a distance of 700 mm from the sample and at the same distance from the detector to provide focusing geometry. Two sets of slits were positioned before and after the analyzer to prevent unwanted radiation from entering the detector. The incident x-ray beam was collimated to 0.5×0.5 mm^2. Another slit was positioned between the graphite analyzer and the detector; it allowed for only an 89-eV energy band pass, sufficient for complete suppression of the x-ray fluorescence above the absorption edge. Studies were performed near the Pb L_{III} absorption edge (13.035 keV) on diffuse 1/2(h,k,l) type superlattice reflections (h, k, and l are odd integers). DAFS-type measurements were performed by collecting diffracted intensity via continuous energy scans at a constant Q point of interest in the reciprocal space. Diffracted intensity was detected with an Oxford scintillation detector. The resolution for energy scans was 2 eV. The fluorescence level was measured by a separate stationary pinhole detector positioned near the surface of the sample. Additional measurements were performed by measuring the full reflection profile in the reflecting θ/2θ bisecting geometry with x-ray energies in a range of 12.9-13.2 keV.

Results

Data collected from the energy scan at constant Q= (2.5, 2.5, 2,5) are shown in Fig. 1. This value of Q corresponds to the peak maximum of the 1/2(555) superlattice peak. The 1/2(h,k,l) peaks are commonly referred to as F spots in the literature [3].

Note that x-ray fluorescence is completely suppressed at the energies above the absorption edge (13.035 keV), and only elastically scattered radiation is detected. The fluorescence signal, collected by a separate detector, was used for linear absorption coefficient calculations. The fluorescence signal is shown in Fig. 2. Calculated μ from Cromer-Liberman formalism is shown by the dashed line. The step height was used to scale the fluorescence intensity in units of cm^{-1}. Calculated μ from James formalism with a width damping coefficient of k= 5 eV is shown by the solid line. The data shown in Fig. 1 were corrected for absorption by multiplying them by the

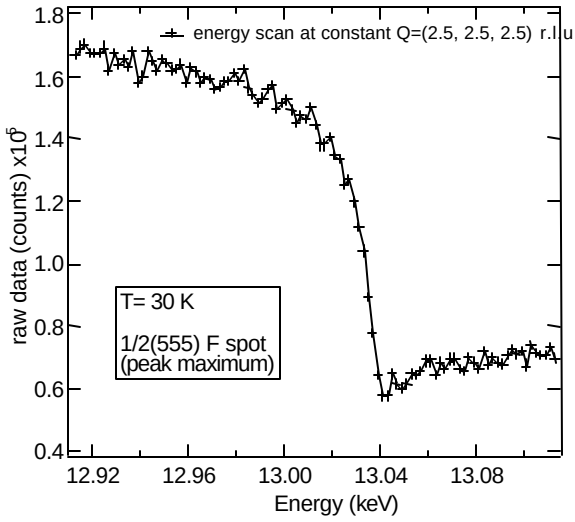

FIG. 1. Energy scan at Q = (2.5, 2.5, 2.5) reciprocal lattice unit (rlu).

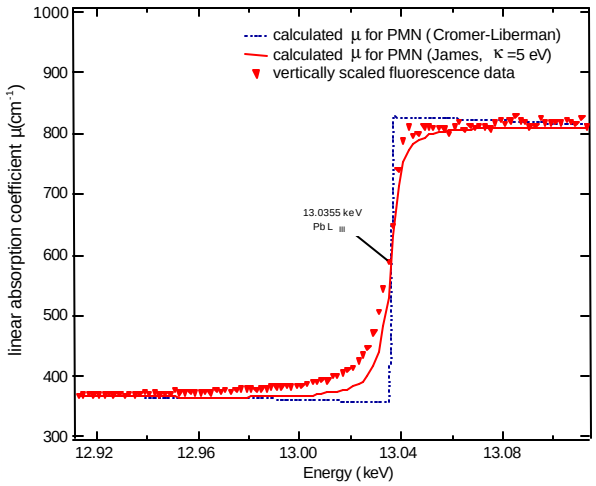

FIG. 2. Calculated linear absorption coefficient m from fluorescence measurements by a separate detector.

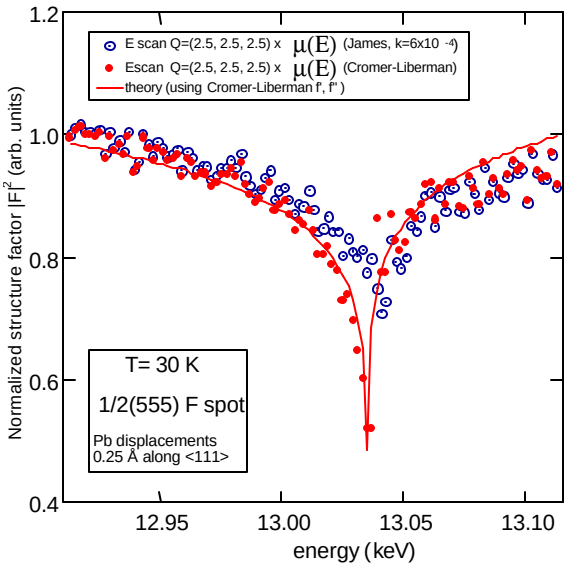

FIG. 3. Results after correction for absorption data and fitted energy dependence of the structure factor.

calculated linear absorption coefficients from Fig. 2. Results of such correction, with μ calculated from Cromer-Liberman and James formalism, are displayed with solid and empty circles, respectively (Fig. 3). The energy dependence of the structure factor was modeled by assuming a Pb displacement pattern alternating every other unit cell along the <111> direction. Several different reflections, such as 1/2(333), 1/2(555), and 1/2(777), were used to fit the data with Pb displacement as an adjustable fitting parameter. Best fit was achieved for all the reflections with 0.25-Å displacements. The calculated energy dependence of the structure factor is shown by the solid line in Fig. 2.

Discussion

The 1/2(h,k,l) superlattice reflections are more than 10^6 orders of magnitude weaker than typical fundamental Bragg reflections in PMN. PMN has a perovkite ABO_3 structure, where the Pb atoms occupy A sites and where B sites are filled with a Nb/Mg mixture. B-site Nb/Mg chemical ordering occurs in small nanodomains with an average size of 50 Å. This type of ordering doubles the unit cell in the <111> direction, which leads to the appearance of the corresponding superlattice reflections (e.g., F spots). It is unlikely that Pb atoms can occupy B sites because of atomic size considerations. Therefore, they can only contribute to the structure factor of the F spots via correlated displacements, which would double the unit cell in <111> [4]. This type of displacement can be constructed by displacing Pb atoms in the anti-parallel fashion in every other unit cell along the <111> direction [5, 6]. Displacements with a magnitude of 0.25 Å were estimated from the experimental results presented in this work. The presence of such anti-parallel Pb displacements may be important in explaining PMN relaxors in terms of competing interaction that prevent the establishment of long-range ferroelectric order [5].

Acknowledgments

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