Anisotropic XANES and Anomalous X-ray Dispersion in Ferroelectric $KNbO_3$

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Introduction

It is well known that strong ferroelectricity in transition metal oxides originates from the electronic polarizability due to covalent bonding. However, there are few direct measurements of the electronic contribution. The purpose of this series of measurements is to determine the electronic polarization in the ferroelectric state, using anomalous x-ray scattering initially and inelastic x-ray scattering later. Preliminary experiments were carried out at the CMC-CAT beamline on a model system, a single-crystal ferroelectric potassium niobate, $KNbO_3$. These measurements revealed polarization-dependent anisotropy in XANES and anomalous dispersion associated with the d-orbitals of Nb.

Methods and Materials

Potassium niobate is a strong ferroelectric with a Curie temperature of 708K, and therefore exhibits a strong directional bonding between niobium and oxygen. Its structure at room temperature is orthorhombic. Niobium-oxygen hybridization in the ferroelectric state is associated with the formation of bonding states along the *a*- and *c*-axes in the *a*-*c* plane. The *b*-axis Nb-O bond is nonbonding (purely ionic). To probe the hybridized niobium-oxygen states the absorption and scattering measurements were performed by scanning the incident x-ray energy through the K-edge of niobium. By rotating the single crystal around the *c*-axis we can make the incident x-ray polarization parallel either to the bonding *a*-axis or the nonbonding *b*-axis. X-ray absorption was measured in the fluorescence mode, with the incident beam nearly normal to the sample surface and the detector making shallow angle with the surface, so that the change in the penetration depth will not affect the fluorescence yield.

Results and Discussion

From the absorption coefficient, we determined the real and the imaginary parts of the anomalous dispersion using the Kramers-Krönig analysis, as shown in Fig. 1. Strong anisotropy in both f' and f" is obvious. In order to determine f' directly, we measured the thermal diffuse scattering, since the Bragg peaks were highly irregular in shape at such high Q resolution, and it was difficult to integrate the intensity over the Bragg peak. The thermal diffuse scattering data collected near several Bragg peaks demonstrated polarization-dependent anisotropy of f'. For instance, the energy dependence of f' measured near the (006) Bragg peak and presented in Fig. 2 exhibits a clear difference between the sets of data taken with the x-ray polarization parallel to the a- and b-axes. Similar polarization-dependent anisotropy was observed for the data collected near other Bragg reflections, such as (008), (606), and (046). After completing the measurements of anomalous dispersion near the K-edge of niobium in KNbO3, we will proceed to the study of the more complex $Pb(Nb,Zr)O_3$-$PbTiO_3$ (PNZ-PT), which is of higher technological importance. Single crystals of PNZ-PT shows piezoelectric strain an order of magnitude larger than for the ceramics used today and are extremely promising materials for piezoelectric applications.

Acknowledgments

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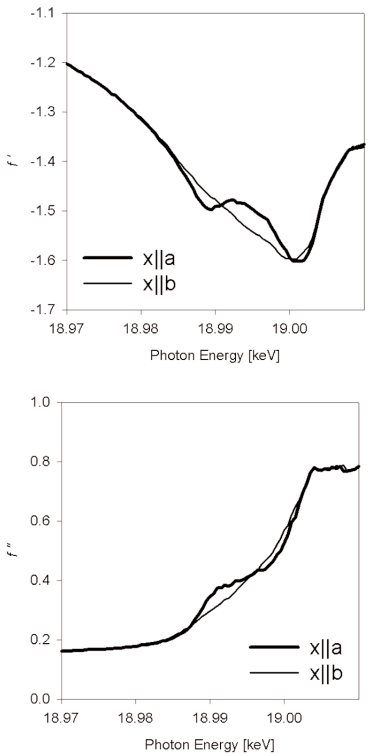

FIG. 1. Anisotropic anomalous dispersion f' and f" of Nb in $KNbO_3$ determined from the absorption measurement.

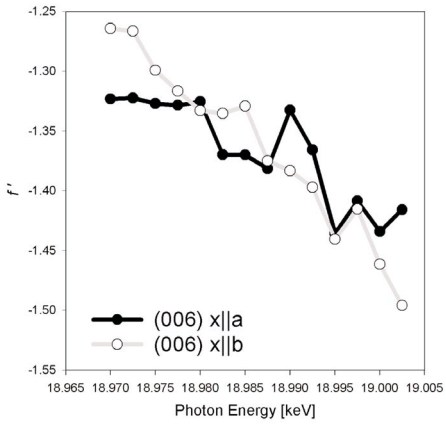

FIG. 2. Anisotropic anomalous dispersion f' of Nb in $KNbO_3$ determined from the thermal diffuse scattering measurement near the (006) Bragg peak.