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Use of X-ray Anomalous Dispersion Effects for Structure Investigation

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Effects of X-ray anomalous dispersion, in particular on superlattice diffraction, have been examined for the antiferroelectric superstructure determination of $PbZrO_3$ single crystal: It is found that Zr atom displaces in a manner of anti-phase pattern along z, while Pb atom shows displacement only on xy plane. On the basis of the information on the displacement patterns, the structure determination has been carried: the superstructure, which is consistent with the results of X-ray anomalous dispersion effect, is determined with R=0.047. As new applications of X-ray anomalous dispersion effect for structure investigation, trial measurements of diffraction anomalous fine structure (DAFS) on satellite diffraction of incommensurately modulated structure of Rb_2ZnCl_4, and of small angle X-ray scattering of Cu ionized NIPA-Gel material have been made.
Key Words: X-ray anomalous dispersion effect, structure determination, DAFS, FRED

1. INTRODUCTION

Many applications of X-ray anomalous dispersion effect have recently been available for structure investigation using synchrotron radiation. A typical technique, for example, is well known as EXAFS method for not only solids but also liquid materials: the technique has been established to local structure determination around the absorbing atoms which exhibit X-ray anomalous dispersion effect at the incident X-ray energy. For crystalline materials, on the other hand, several techniques, such as "Diffraction Anomalous Fine Structure (DAFS)" and "Forbidden Reflection near Edge Diffraction (FRED)", have being studied as new methods of structure determination. In this paper, at first, we report an application of X-ray anomalous dispersion effect for the determination of complicated superstructure which is hard to be solved by conventional method. Then, recent trial investigations of incommensurate structure analysis using DAFS measurements on satellite diffraction, and of metal-ionized Gel structure analysis using small angle X-ray scattering will be discussed.

2. SUPERSTRUCTURE OF $PbZrO_3$

Since the discovery of antiferroelectricity of $PbZrO_3$[1], many attempts on the superstructure determination have been carried. In spite of the X-ray[2], neutron[3,4,5,6] and electron[7,8] diffraction studies, the superstructure has been ambiguous for more than forty years. Recently, Glazer *et al.* succeeded to grow a monodomain single crystal, and they have done X-ray structure determination[9]. The superstructure was determined with R=0.06: Pb atom has antiferroelectric displacements on xy plane, and the stacking of the pattern along z is out-of-phase. The Zr atom shows antiferroelectric displacement on xy plane, too, but in contrast with Pb, the stacking is in-phase along z. They also suggested that the structure consists of random distribution of two substructures which are related by translation symmetry with the amount of c/2. The results contradicts with those reported in the literature.

Though the intensities of the superlattice diffraction are straightforwardly contributed by the patterns of the displacements of heavy atoms, problem is that the intensity, in particular on superlattice diffraction with the index l odd, is extremely weak for the structure determination. In order to obtain information on the exact displacement patterns, a use of X-ray anomalous dispersion effect is effective. In Fig.1, calculated structure factors of 265, 450, superlattice diffractions,

and 0 0 12, fundamental diffraction, are shown as a function of incident X-ray energy around Pb L and Zr K edges: the calculation is based on the Glazer[9] model. In accordance with the Zr displacement pattern, no dispersion effect appears only on 265 diffraction around Zr K absorption edge. Details are given in the reference[10].

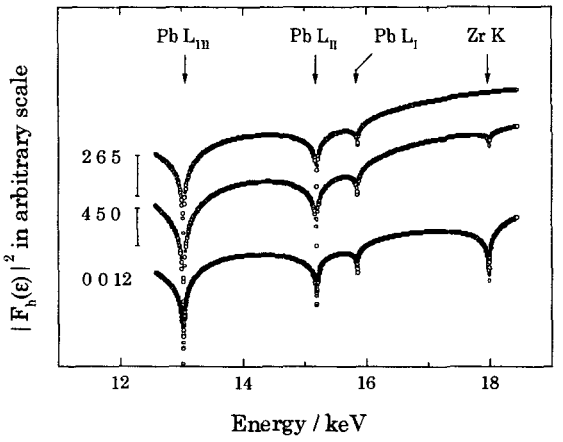

Fig.1 Calculation of the squared structure factor, on the basis of the Glazer model [9], for the superlattice diffractions, 265, 450, and fundamental diffraction 0 0 12 as a function of incident X-ray energy. The bars on left correspond to a relative change of 10% in the structure factor of the superlattice diffractions.

3. EXPERIMENTAL AND RESULTS

Intensity measurements have been made on 421, 265, 225 and 227 superlattice diffractions with *l* odd, at BL-1F beam line of Doris III synchrotron radiation facility in DESY, Germany. Results are shown in Fig.2. As clearly shown in the figure, all the diffractions show remarkable changes in intensity around both Pb L_{III} and Zr K edges, in contrast with the results shown in Fig.1. This directly indicates that the both Pb and Zr atoms contribute to the formation of the superstructure, and the result requires reinvestigation of the structure. The structure determination has been carried only with the intensities of superlattice diffraction collected with 0.45 Å synchrotron radiation, in order to avoid the effects of complicated domain structure and the strong absorption. The measurements were made at Bl-10A beam line in PF, Tsukuba. Final result with R=0.047 was obtained and the results of atomic coordinates are listed in Table I [11]: Pb shows antiferroelectric type of displacements

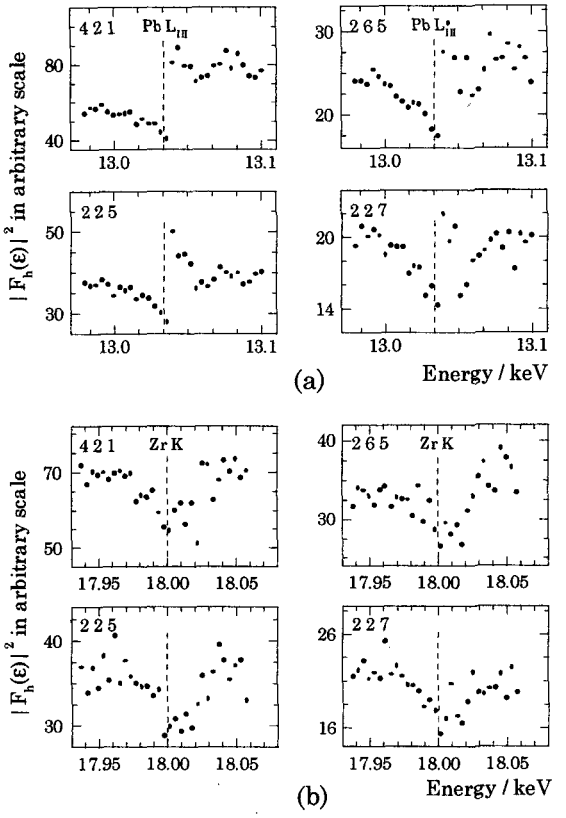

Fig.2 Observed squared structure factor of superlattice diffractions. (a) around Pb L_{III} and (b) around Zr K absorption edge. The scale for the structure factor is arbitrary, but common for all the diffractions.

Table I Atomic coordinates and temperature factors of the superstructure of $PbZrO_3$.

Space group *Pbam*

a = 5.8884(19), b = 11.771(4), c = 8.226(3) Å, Z = 8.

	Site	x	y	z
Pb1	4g	0.7085(3)	0.1300(3)	0
Pb2	4h	0.7117(4)	0.1246(4)	0.5
Zr	8i	0.2423(3)	0.1242(3)	0.253(6)
O1	4g	0.291(2)	0.1009(12)	0
O2	4h	0.2761(2)	0.1585(16)	0.5
O3	8i	0.0284(12)	0.2606(5)	0.2207(11)
O4	4f	0.5	0	0.302(2)
O5	4e	0	0	0.282(2)

on *xy* plane and the stacking of the displacement pattern is out-of-phase along *z*. On the other hand, Zr has anti-phase displacements to *z*, while the stacking of displacements on *xy* plane is in-phase. Consequently, both of heavy atoms contribute to the formation of the superstructure in different manners of the displacement pattern. Recently, Corker *et al.*[12] made the structure determination with the data collected at low temperature, and obtained the same results as that in present study.

4. NEW APPLICATIONS

As trial investigations, Diffraction Anomalous Fine Structure (DAFS) [13,14] were measured on a typical incommensurate structure of Rb_2ZnCl_4. Examples of measured DAFS signals around Zn K absorption edge are shown in Fig.3, respectively on fundamental, 633, satellite, 721, and forbidden, 041, diffractions. The measurements were made at BL-14A beam line at PF, Tsukuba. For the fundamental and satellite diffractions, the intensity oscillations due to DAFS phenomena are clearly observed in the incident X-ray energy region higher than the absorption edge. It is noted that the DAFS oscillations seem to be in opposite phases on respectively fundamental and satellite diffractions, in the region from the edge to 9800 eV, and to be in-phase in the region higher than 9800 eV. This informs us a detailed local structure around Zn ion in the incommensurately modulated structure. In addition, it is noted that the intensity of the fundamental diffraction is strongly affected by the incident X-ray energy in the region lower than the absorption edge, and, in contrast, the intensity of the satellite diffraction is not affected. The results are in accordance with the fact that the satellite diffraction consists of incommensurate modulation of only Cl ions. For the forbidden diffraction, the "Forbidden Reflection near Edge Diffraction (FRED)" [15,16,17] intensity due to "Anisotropy of the Tensor of Susceptivility (ATS)" [18,19,20] clearly appears around the absorption edge, instead of DAFS signal. The intensity informs us the X-ray resonant interaction with the anisotropy of the orbit state of Zn ion in the incommensurate modulation. The intensity peak at 9.95 keV can not be attributed to FRED, but may be done to simultaneous diffraction. The theoretical discussions are given in the reference [21] and detailed analysis of the present measurements will be given in elsewhere.

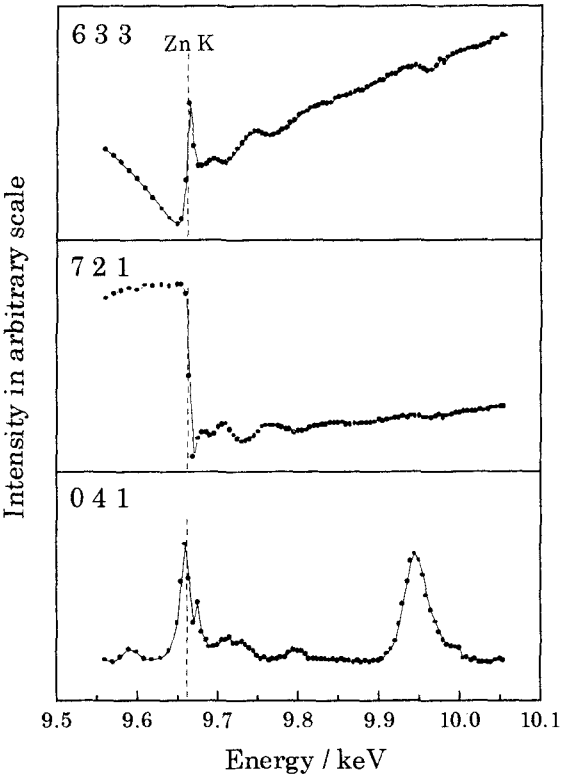

Fig.3 Observed DAFS signals on fundamental 633 and satellite 721 diffractions of Rb_2ZnCl_4. For the forbidden diffraction, 041, FRED intensity is observed around the absorption edge.

Finally, an application of the X-ray anomalous dispersion effect on small angle X-ray scattering measurements for the meso-scorpic structure investigation of Cu ionized NIPA-Gel is mentioned. Fig.4 shows small angle scattering intensities measured around Cu K absorption edge. The measurements were made at BL-10C beam line in PF, Tsukuba. Owing to the anomalous dispersion effect of Cu ion, the intensity is affected by the incident X-ray energy: the intensity changes are obvious only around the small angle corresponds to 200 Å distance at where the first mesoscorpic condensation of NIPA-Gel molecule is constructed. The results guarantee that the Cu ions are adsorbed in the same scale of the meso-scorpic molecule structure of NIPA-Gel and that there is no more smaller scale of the ion condensation. For the larger structure, the ultra-small angle scattering experiments is required in the further investigations.

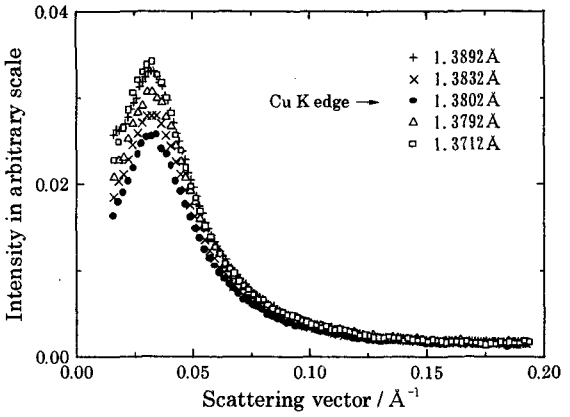

Fig.4 Observed small angle X-ray scattering intensity from Cu ionized NIPA-Gel. Intensity changes due to the anomalous dispersion effect of Cu ion are obvious on the intensity peaks at 0.03 $Å^{-1}$.

5. SUMMARY

Use of X-ray anomalous dispersion effects is provides us a new method of structure investigation which has not been realized by conventional method. The technique is effective for the complicated structure determination such as super and incommensurate structures, and moreover, for the local structure analysis of around the selected kind of element in materials. The technique will be further developed by using synchrotron radiation, and will be established as a conventional way for the structure determination.

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