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Use of X-ray Anomalous Dispersion: the Superstructure of $PbZrO_3$

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Abstract

Intensity measurements of several superlattice reflections of lead zirconate, $PbZrO_3$, have been made on single-crystal specimens as a function of incident X-ray energy around the Pb L_{III} and Zr K absorption edges. Anomalies in the squared structure factor $|F(hkl)|^2$ of superlattice reflections with l odd, and of those with l even, are observed at both the absorption edges. This indicates that both Pb and Zr atoms show an out-of-phase type of displacement, not only on the xy plane but also along the z axis in the orthorhombic cell. The results of the Zr displacement are in contradiction with the models in the literature. It is shown that the use of X-ray anomalous dispersion is effective to obtain information on the atomic displacement and to investigate the superstructure.

1. Introduction

In spite of the many diffraction studies that followed the discovery of the antiferroelectric phase transition in $PbZrO_3$ (Sawaguchi, Maniwa & Hoshino, 1951), the superstructure in the low-temperature phase is still ambiguous. By means of X-ray and neutron diffraction, Jona, Shirane, Mazzi & Pepinsky (1957) suggested the space group *Pba*2 and proposed a model structure (the Jona model). More recently, convergent-beam electron diffraction and neutron diffraction experiments have been carried out by Tanaka, Saito & Tsuzuki (1982*a*) and Fujishita & Hoshino (1984), respectively; they suggested the space group *Pbam*. A serious problem in these studies was that single crystals were available only in the form of fine grains; the X-ray intensity of

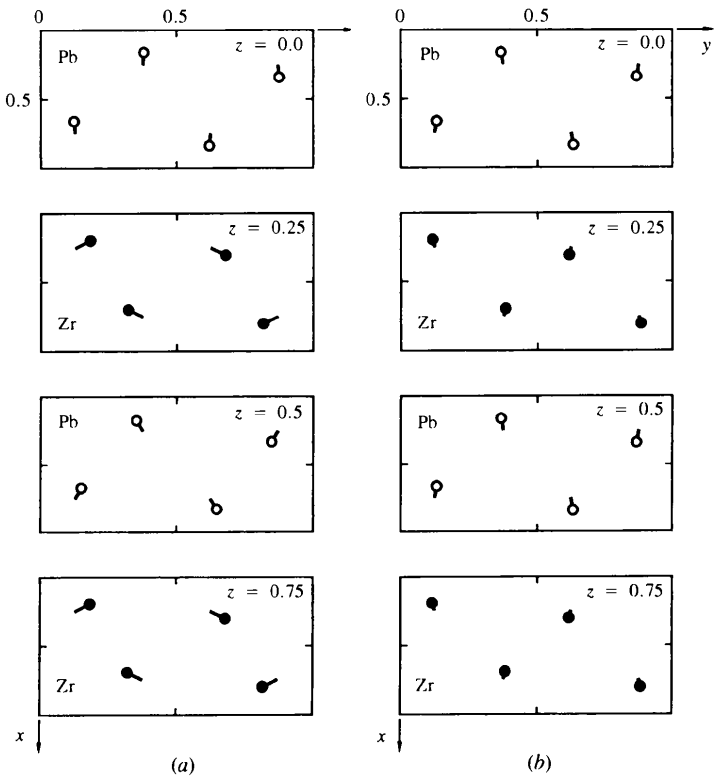

Fig. 1. Displacement of Pb (open circles) and Zr (full circles) atoms is shown in an exaggerated manner: (*a*) the Glazer model and (*b*) the Jona model. The tip of the mark indicates the position in the cubic perovskite structure.

superlattice reflections was too weak to be used for determining the superstructure, while neutron diffraction with a powder specimen was not appropriate for space-group determination. Glazer, Roleder & Dec (1993) succeeded in growing a large monodomain single crystal and tried an X-ray structure determination. They proposed a model structure (the Glazer model) that consists of two types of substructures; the space group was assigned to be *Pbam*.

It is to be noted that, even for the heavy elements Pb and Zr, the atomic coordinates in the model structures mentioned above are quite different. For comparison, the displacements of Pb and Zr are shown schematically in Figs. 1(*a*) and 1(*b*) for the Glazer and Jona models, respectively. In the following we assume the orthorhombic cell, the lattice constants of which are related by $a = 2^{1/2}a_p$, $b = 2 \times 2^{1/2}b_p$, $c = 2c_p$; a, b and c being 5.876, 11.771 and 8.219 Å, respectively. Here a_p, b_p and c_p denote lattice constants of cubic perovskite structure. Here, Pb (open circles) are on the xy planes at $z = 0$ and 0.5, and Zr (full circles) at $z = 0.25$ and 0.75; the tail of a circle indicates the displacement from the position in the cubic structure. In (*a*) the displacement pattern of Zr on the xy plane shows the in-phase sequence along z, while that of Pb is the out-of-phase sequence; in the case of (*b*), on the other hand, the patterns of both Pb and Zr show the in-phase sequence. This difference between the two models directly indicates the difference in the construction of the superstructure along the z direction: in (*a*) the superstructure consists of the displacements not only of O atoms but also of Pb atoms, while in the case of (*b*) only O atoms participate. Since the intensity of superlattice reflections with l odd is extremely weak, it is particularly difficult for the conventional structure determination to specify the correct superstructure; in other words, the R factor is only negligibly affected by the difference between the displacement sequence along **z** in these models.

In the present paper we propose a new method to confirm the type of the displacements of heavy elements using the effect of X-ray anomalous dispersions. According to the expression for the squared structure factor given by Soejima & Fischer (1988), that of the superlattice reflection $|F_\mathbf{h}|^2$ can be given as follows by taking account of the atomic displacement and anomalous dispersion:

$$
\begin{aligned}
|F_\mathbf{h}|^2 = {} & (a_e^2 + b_e^2) \sum_{t_e}^{k} \sum_{t_e}^{j} [\cos \omega(r_k - r_j + \Delta_k - \Delta_j) \\
& - 2 \cos \omega(r_k - r_j + \Delta_{2k} - \Delta_j) \\
& + \cos \omega(r_k - r_j + \Delta_{2k} - \Delta_{2j})] \\
& + 2(a_e a_n + b_e b_n) \sum_{t_e}^{k} \sum_{t_n}^{j} [\cos \omega(r_k - r_j + \Delta_k - \Delta_j) \\
& - \cos \omega(r_k - r_j + \Delta_{2k} - \Delta_j) \\
& - \cos \omega(r_k - r_j + \Delta_k - \Delta_{2j}) \\
& + \cos \omega(r_k - r_j + \Delta_{2k} - \Delta_{2j})] \\
& + (a_n^2 + b_n^2) \sum_{t_n}^{k} \sum_{t_n}^{j} [\cos \omega(r_k - r_j + \Delta_k - \Delta_j) \\
& - 2 \cos \omega(r_k - r_j + \Delta_{2k} - \Delta_j) \\
& + \cos \omega(r_k - r_j + \Delta_{2k} - \Delta_{2j})] \\
& + 2(a_e b_n - b_e a_n) \sum_{t_e}^{k} \sum_{t_n}^{j} [\sin \omega(r_k - r_j + \Delta_k - \Delta_j) \\
& - \sin \omega(r_k - r_j + \Delta_{2k} - \Delta_j) \\
& - \sin \omega(r_k - r_j + \Delta_k - \Delta_{2j}) \\
& + \sin \omega(r_k - r_j + \Delta_{2k} - \Delta_{2j})],
\end{aligned}
$$

where $a = (f^o + f')T$ (a real part of the form factor), $b = f''T$ (an imaginary part of the form factor), $T = \exp[-B(\sin\theta/\lambda)^2]$ (the Debye–Waller factor) $r_i = (x_i, y_i, z_i)$ (the coordinate of the ith atom), and $\omega = 2\pi\mathbf{h}$. Here, Δ_i is a small displacement of the ith atom from the position of higher symmetry r_i. Since the unit cell of the superstructure is assumed to be twice as large as that of the fundamental lattice, we write the coordinate of the $2i$-th atom as $r_{2i} = (r_i + \frac{1}{2}) + \Delta_{2i}$. The subscripts e and n denote 'edge' and 'normal', respectively; a_e and b_e, respectively, indicate the real and imaginary parts of the form factor of the atom with the absorption edge at or near the incident beam energy (edge atom). In a similar way a_n and b_n are relevant to the atom with no dispersion effect (normal atom). The edge and normal atoms that have the displacement in the superstructure are denoted by t_e and t_n, respectively.

The equation consists of the summation over t_e and t_n: this corresponds to the fact that the superlattice reflection consists of the sum of Fourier components of the displacement. It is clear from the equation that $|F_\mathbf{h}|^2$ is independent of incident energy if there is no t_e atom: $|F_\mathbf{h}|^2$ then consists of the sum over only t_n with the coefficient $(a_n^2 + b_n^2)$, which is independent of incident energy. In contrast, for the t_e atom, owing to changes in the anomalous dispersion terms f_e' and f_e'', a change in the squared structure factor as a function of energy ε, $|F_\mathbf{h}(\varepsilon)|^2$, is expected at and near the absorption edge. This behaviour is useful to investigate the superstructure of $PbZrO_3$, in particular, to determine the pattern of cation displacements.

Since we assume the orthorhombic structure, fundamental reflections are those with $h =$ even and $k = 4n$ or $h =$ odd and $k = 4n + 2$, with $l =$ even, $n =$ integer; all others are superlattice reflections. For the out-of-phase sequence of the displacement pattern along the z axis, $|F_\mathbf{h}(\varepsilon)|^2$ with l odd is concerned. According to Fig. 1, a change in $|F_\mathbf{h}(\varepsilon)|^2$ with l odd

is expected to be observed only at the Pb edge for the Glazer model and at neither of the Pb and Zr edges for the Jona model. In both the models, on the other hand, $|F_h(\varepsilon)|^2$ of superlattice reflections with l even which originate in the cation displacement on the xy plane and that of all the fundamental reflections must show a change at both absorption edges. As examples, the results of numerical calculations of $|F_h(\varepsilon)|^2$ for the superlattice reflections 265 and 450, and for the fundamental reflection 0,0,12, are shown in Fig. 2 for the Glazer model (*a*) and for the Jona model (*b*), in the energy region covering the Pb L_{III} and Zr K edges. Here, as for the Glazer model, we assume that the volumes of the two substructures are equal to each other. The anomalous dispersion terms f' and f'' used in the calculation are those given by Sasaki (1989). As mentioned above, it is clear that $|F_h(\varepsilon)|^2$ of 265 shows the characteristic difference between the two models, while those of 450 and 0,0,12 behave in a similar manner.

As indicated in Fig. 2, a change in $|F_h(\varepsilon)|^2$ of superlattice reflections around the absorption edges is expected to be of the order of 10% at the Pb L_{III} edge and 1% at the Zr K edge; the change, therefore, is detectable. The measurement can be made by means of conventional X-ray diffractometry using a four-circle goniometer. It is essential, however, that the incident beam energy must be tunable and that the incident intensity must be strong enough for measuring extremely weak reflections. These conditions are easily realized by the use of synchrotron radiation.

2. Experimental

More than 20 specimens of $PbZrO_3$ with flat surfaces and no cracks were selected from thousands of fine grains; each grain was nearly cube-shaped and $\sim 50 \times 50 \times 50\,\mu m$ in dimensions. One specimen was finally chosen for the intensity measurement after being examined, in particular, in connection with a domain structure by Weissenberg photography.

Intensity measurements of superlattice reflections with l odd, 421, 265, 225 and 227, and those with l even, 450, 1,12,0, 1,11,4 and 2,15,0, were made as a function of incident beam energy around the Pb L_{III} and Zr K edges. The integrated intensity was determined in ω scans of a four-circle diffractometer on beamline F1 at DORIS III, DESY. The incident energy was tuned at intervals of 0.004 keV by using silicon 111 of a double-crystal monochromator, the relative resolution $\Delta\varepsilon/\varepsilon$ being $4\text{–}7 \times 10^{-4}$. The higher harmonics of the monochromatized beam with energies 3ε, 6ε, *etc.* were eliminated by slightly mismatching the second monochromator crystal to the Bragg condition. The squared structure factor was deduced from the integrated intensity after correction for the brightness of incident spectrum, Lorentz factor and absorption, at each incident energy.

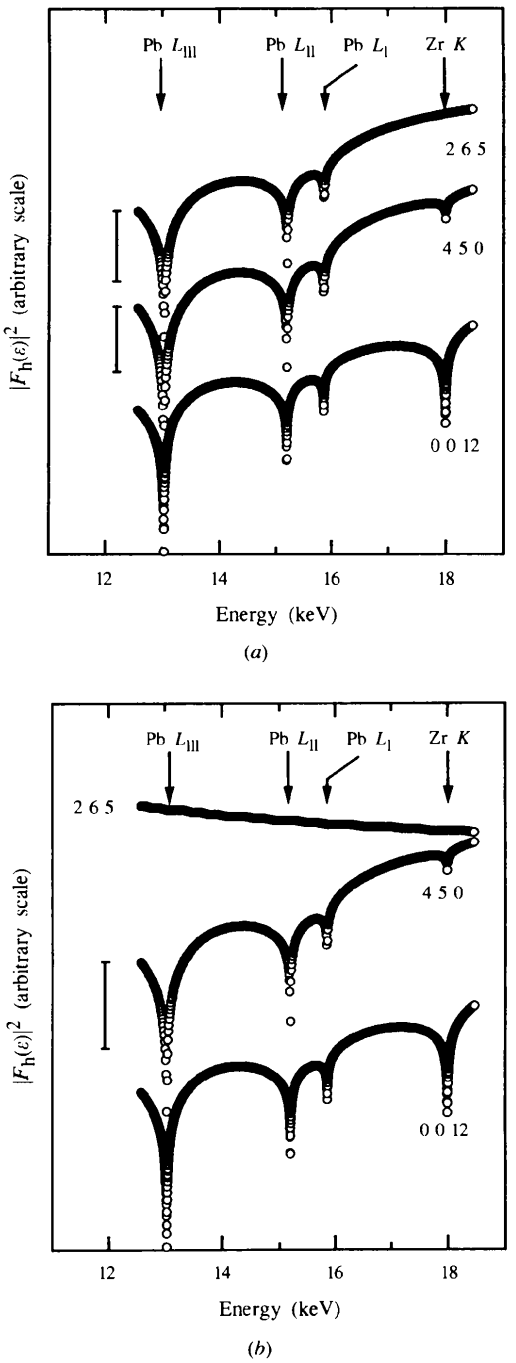

Fig. 2. Calculated $|F_h(\varepsilon)|^2$ based on (*a*) the Glazer model and (*b*) the Jona model. Examples are given for the 265 and 450 superlattice reflections and for the 0,0,12 fundamental reflection. The bars on the left correspond to a relative change of 10% in $|F_h|^2$ of the superlattice reflections.

3. Results

3.1. $|F_h(\varepsilon)|^2$ *at the Pb* L_{III} *edge*

The observed $|F_h(\varepsilon)|^2$ is shown in Figs. 3(*a*) and 3(*b*) for the superlattice reflections with l = odd and even, respectively. The fact that the former reflections show remarkable changes in $|F_h(\varepsilon)|^2$ around the Pb L_{III} edge indicates that Pb atoms have an out-of-phase type of displacement along the z axis. This agrees with the Glazer model, but not with the Jona model. The situation can be understood by referring to Figs. 2(*a*) and 2(*b*). The results for the latter reflections given in (*b*) also show changes around the edge; it is, therefore, obvious that Pb atoms participate in the formation of the superstructure along both x and y. This is consistent with both the Glazer and Jona models.

3.2. $|F_h(\varepsilon)|^2$ *at the Zr K edge*

In Figs. 4(*a*) and (*b*) the observed $|F_h(\varepsilon)|^2$ of the superlattice reflections around the Zr K edge is shown. All the reflections show changes of the same order of relative magnitude; the results show that Zr

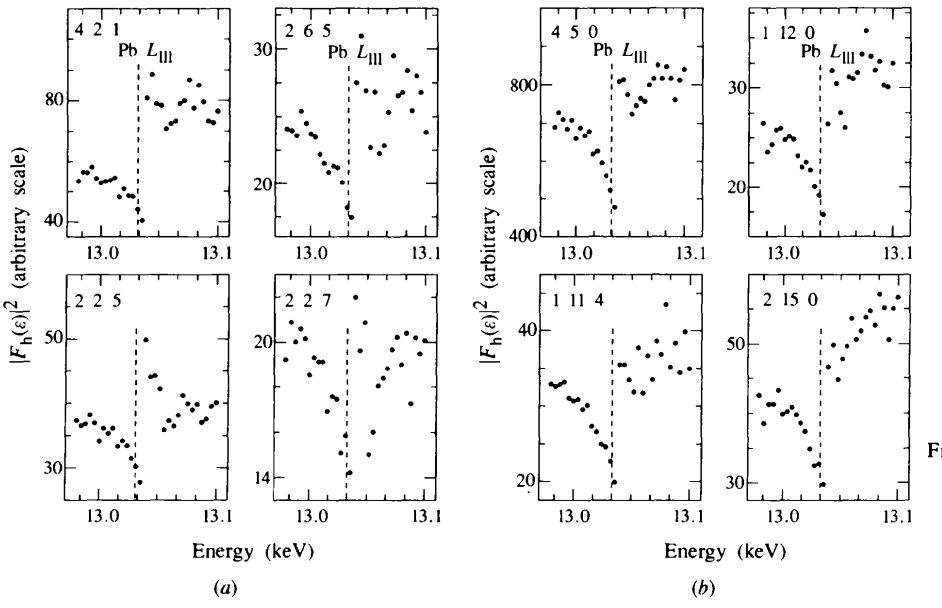

Fig. 3. Observed $|F_h(\varepsilon)|^2$ of superlattice reflections around the Pb L_{III} edge: (*a*) for the reflections with l odd and (*b*) for those with l even. The scale for $|F_h(\varepsilon)|^2$ is arbitrary, but is common for all the reflections.

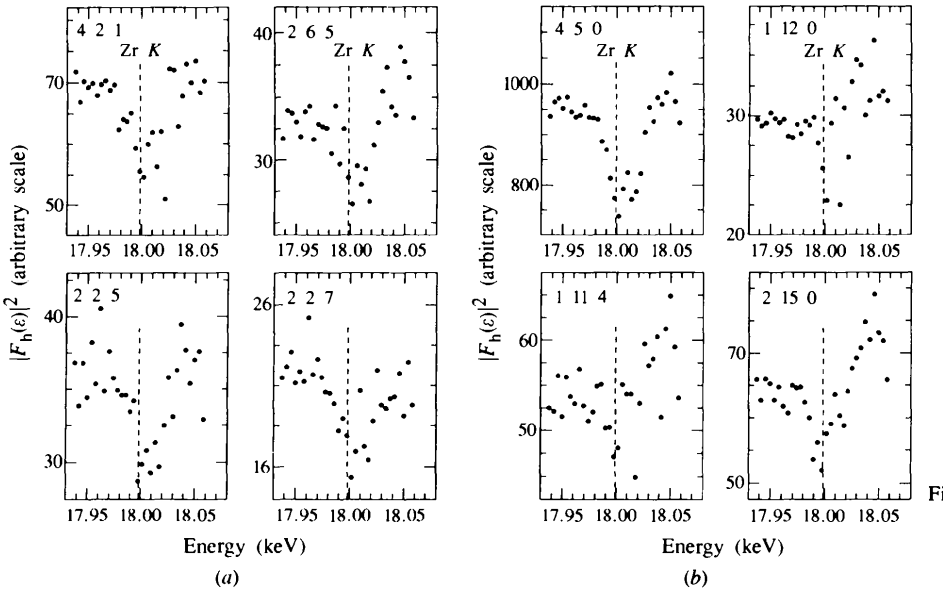

Fig. 4. Observed $|F_h(\varepsilon)|^2$ of superlattice reflections around the Zr K edge: (*a*) for reflections with l odd and (*b*) for those with l even. The scale for $|F_h(\varepsilon)|^2$ is as in Fig. 3.

atoms participate in the formation of the superstructure along z. This is not consistent with either of the Glazer and Jona models.

4. Discussion

One difficulty in the superstructure determination is that the intensity of superlattice reflections that directly results from the small displacement of the atoms is generally very weak. In the case of $PbZrO_3$ the difficulty is particularly serious. The intensity of superlattice reflections is extremely weak; a typical ratio of intensities of weak superlattice reflections, strong superlattice reflections and strong fundamental reflections is 1:400:7200. Therefore, it is very hard to determine the atomic displacement by means of a conventional refinement procedure that minimizes the R factor. On the other hand, as shown in Figs. 3 and 4, the effect of X-ray anomalous dispersion on the structure factor is large enough to be detected, even though the intensity itself is extremely weak: the relative changes in $|F_h|^2$ at the absorption edges Pb L_{III} and Zr K reach 30 and 20%, respectively. The effect of anomalous dispersion on the structure factor is so remarkable that the use of the effect is suitable for obtaining information on the atomic displacement in the superstructure.

Another problem for the structure determination is the effect of complicated domain structures. At the cubic-to-orthorhombic phase transition six types of domain may appear; they are classified into three groups by the direction of the z axis being parallel to the axes of the cubic perovskite c_p, a_p and b_p. For each group there are two types of domains that are related by 90° rotation around the z axis. These domains were directly observed by means of electron microscopy (Tanaka, Saito & Tsuzuki, 1982*b*), and termed the 90 or 60° domains; the 180° domain was also found. However, we cannot distinguish the 180° domains by X-ray diffraction. Since fundamental reflections of these domains are generally superposed, it is essential to know the relative volume of these domains when we determine the crystal structure. Some of the superlattice reflections are not affected by those of other domains; such reflections are useful for the determination of the domain population (Hidaka, 1975; Hidaka & Ono, 1977). In the case of $PbZrO_3$, unfortunately, it is hard to determine the domain population in this way, because the incident X-rays are hindered from passing through the specimen by large absorption: we observe the domain population only on the surface of the specimen where the X-ray impinges. Now we examine the effect of these domains on the conclusion that is based on the results given in Figs. 3 and 4, and is given in the preceding section. It is easy to verify the relation as follows: any superlattice reflection with l odd may be superposed by superlattice reflections of other types of domains, but all must be with l odd. A similar relation is valid for superlattice reflections with l even. Therefore, there is no ambiguity in deducing the conclusion mentioned above. It is to be noted that superlattice reflections with $k \neq 2n$ are free from the superposition of others; unfortunately, since those with l odd are extremely weak, it is not practical to use these reflections. Consequently, reflections given in Figs. 3 and 4 are chosen from those with larger intensities.

The present results require that the contribution of Zr atoms to the formation of the superstructure must be reconsidered. This motivates a precise superstructure determination of $PbZrO_3$, the results of which will be reported elsewhere.

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