# *In-situ* X-ray Diffraction Study of Electric Field Induced Domain Switching and Phase Transition in PZT-5H

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**Abstract**

*In-situ* x-ray experiments were conducted to examine the electric-field-induced phase changes in PZT-5H materials. The x-ray diffraction profiles at different electric field levels were analyzed by peak fitting and used to identify the occurrence of non-180° domain switching and phase transition. We found that, in depolarized samples, there exists a threshold electric field for the phase changes; whereas in polarized samples, no such threshold exists. The profound difference in the diffraction profile changes under positive and negative electric fields in polarized samples is responsible for the asymmetry of piezoelectric effects. Peak fitting results show composition and transition of phases as well as domain switching at different electric field levels. These observations further indicate the importance of residual stresses in materials behaviors.

## I. Introduction

Perovskite ferroelectric/piezoelectric $PbZr_{1-x}Ti_xO_3$ (PZT), $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMN–PT) and $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PZN–PT) have been intensively studied recently. Above the Curie temperature, they all have simple cubic structures, while at lower temperatures, it was believed that they become tetragonal or rhombohedral structures. The composition, x, determines whether a tetragonal or rhombohedral structure is formed at a given temperature. The phase boundary in the phase diagram, which separates tetragonal from rhombohedral region is called the morphotropic phase boundary (MPB)[1]. Recently, Noheda et al. reported a new phase in polycrystalline PZT materials, which belongs to one type of monoclinic phases[2-4]. They suggested that the MPB that was previously believed to separate tetragonal and rhombohedral phases is actually the boundary between tetragonal and monoclinic phases. They also suggested there exist a "morphotropic phase" region between tetragonal and rhombohedral regions in the phase diagram[3]. The new monoclinic phase was also observed by Souza Filho et al.[5].

Extraordinarily strong piezoelectric constants are found mostly in materials with compositions near the MPB. Although the large piezoelectric constants are normally believed to be due to the coexistence of morphotropic phases and the associated phase changes, the underlying mechanisms remain unsettled[6-13]. On the other hand, it has been found that piezoelectric constants exhibit a large nonlinear behavior[14-18]. Above a threshold electric field, the piezoelectric constant increases if the amplitude of the applied electric field increases. The threshold level can be very low or nearly zero[15,16], or can be a finite value[17]. It was also observed that the piezoelectric constant depends on the

direction of a biased electric field, a positive biased electric field results in decreased piezoelectric constants, while a negative biased field results in increased piezoelectric constants[18]. The nonlinear effect was explained by different mechanisms, such as domain wall motion, $90^o$-domain switching, or residual stresses. However, most of the mechanisms are indirectly deduced from the measurements of material's constants. Only a few direct observations on microstructural changes have been made, especially in the case of polycrystalline materials.

Experiments on single crystalline relaxor-based ferroelectric PMN-PT and PZN-PT showed that enhanced and nonlinear piezoelectric coefficients are likely due to the phase transition between rhombohedral and tetragonal phases induced by electric fields[19-20]. A first principle simulation indicated that the phase transition results from an electric field induced polarization rotation[21]. Quantitative experiments on polycrystalline materials are difficult to conduct due to their complex microstructures. However, such experiments can help to identify the mechanisms responsible for the enhanced and nonlinear piezoelectric constants. An x-ray diffraction conducted on polycrystalline PZN-PZT indicated that a large amount of phase transitions between rhombohedral and tetragonal phases and non-$180^o$ domain switching ($90^o$ domain switching for tetragonal phases and $71^o$ or $109^o$ domain switching for rhombohedral phases) are induced by the poling process[8]. However, the result does not provide a direct observation of microstructural changes in a poled sample upon an applied electric field.

PZT-5H is one of the most used polycrystalline PZT materials. Its piezoelectric constants have been studied in detail[16,22]. Some researchers suggested that tetragonal and rhombohedral phases coexist at room temperatures in the PZT materials with

compositions near the MPB[16,23,24]. Non-180° domain switching and phase transition between those two phases, therefore, were believed to be the source of their strong, nonlinear piezoelectric behavior[15]. Other researchers suggested that residual stresses are the real source[16]. The recently modified MPB suggested the coexistence of tetragonal and monoclinic phases in PZT materials near the MPB[3,4]. Some first-principle simulations, however, suggested that the large piezoelectric effects could come from field-induced monoclinic distortions[25,26]. A direct observation seems to provide some evidence for such distortions[11]. But more careful and thorough experiments are needed to confirm the type of those distortions. Therefore, direct observations of electric field induced microstructural changes are critical to clarify the mechanisms responsible for the strong and nonlinear behavior in polycrystalline piezoelectric materials.

In the present paper, *in-situ* x-ray diffraction experiments were performed on a PZT-5H material. Direct observations of non-180° domain switching and phase transition at different electric fields were made for depolarized and polarized samples. Our results provide specific information on the microstructural changes giving rise to the material's piezoelectric properties, and show the effect of residual stresses on the nonlinear piezoelectric behavior.

## II. Experiment

Thin plate specimens of PZT-5H are used in our experiments. The samples have a thickness of 375 μm and in-plane dimensions of 2 cm × 2 cm. The Curie temperature of the material is 220 °C and the coercive field ($E_C$) is 8 KV/cm. All samples are coated with nickel as electrodes on the top and bottom surfaces and poled in their thickness

directions. Some samples were depolarized by submerging them into a silicon–oil bath at 260 $^{o}$C for half an hour, and then cooling down to room temperature gradually. The diffraction patterns of the depolarized samples are close to those of ceramic powder.

Recent research suggested that PZT-5H could have a combination of tetragonal and rhombohedral phases[16] or a combination of tetragonal and monoclinic phases[3,4]. Figure 1 shows the geometries of a tetragonal, a rhombohedral, and a monoclinic unit cell. The lattice angle $\alpha$ for a rhombohedral unit cell is slightly less than 90$^{o}$. The monoclinic unit cell is double in volume compared to a tetragonal unit cell. Its $a_m$ and $b_m$ lie along the tetragonal $[\bar{1}\bar{1}0]$ and $[1\bar{1}0]$ directions, respectively. Its $c_m$ tilts slightly from the [001] direction with the angle $\beta$ between $a_m$ and $c_m$ slightly larger than 90$^{o}$. The polarization directions are along (001) and (111) for tetragonal and rhombohedral unit cells, respectively. The polarization direction can lie anywhere between (001) and (101) in $a_m c_m$ plane for a monoclinic unit cell.

The x-ray diffraction ($2\theta$-$\theta$ scan) is performed with a Rigaku D-Max powder x-ray diffractometer at the Frederick Seitz Materials Research Laboratory at the University of Illinois. The instrument uses copper radiation with lines $K\alpha_1$ and $K\alpha_2$ (wavelength $\lambda_{\alpha_1}$ = 1.5406 Å and $\lambda_{\alpha_2}$ = 1.5444 Å). The top and bottom electrodes of the samples are connected to a DC power supply. The x-ray diffraction is measured *in-situ* under applied electric fields. Because of their morphotropic and polycrystalline microstructures, diffraction patterns are rather complicated. A moderate-speed scan is first conducted for a large $2\theta$ range to locate approximately the peak positions. Slow scans are then conducted for individual peaks in a 3$^{o}$-4$^{o}$ $2\theta$ range. The effect of the electric field on diffraction

peaks is studied first. Domain and phase changes are further studied by peak fitting. Those peaks are carefully fitted by a peak fitting program Xfit-Koalariet developed by Cheary and Coelho[27]. The peaks are fitted by a pseudo-Voigt (PV) shape function and the two-wavelength effect is taken into account. Furthermore, the anisotropic peak width and coexisting phases are also considered[3,4].

## III. Results and Discussions

### 3.1 Effect of Electric Fields on Diffraction Peaks

Figure 2 shows the diffraction profile of a PZT−5H sample over a wide $2\theta$-range, indicating the pseudo-cubic peak locations. Figure 3 shows slow-scan diffraction profiles at pseudo-cubic (111), (200), and (220) regions in a depolarized sample at several applied electric field levels. It clearly shows that there exists a threshold electric field between $.33E_C$ to $.5E_C$ for all peaks. Below the threshold field, the diffraction profiles do not change. Experimental results show that the peaks at other pseudo-cubic regions behave in a similar way.

Figure 4 shows the change of the pseudo-cubic (200) peak in a polarized sample, where a positive electric field is along the poling direction. Unlike the case of a depolarized sample, there is no clear threshold electric field for peak profile change. Under a positive electric field, the change of diffraction profile is very small and gradual. Under a negative electric field, the peak profile changes slowly at low fields and profoundly when $|E| > 0.5E_C$. These observations are consistent with the value ($.5E_C$) observed by Wang et al., in which they applied an electric field perpendicular to the

poling direction and measured strains in both the poling direction and that normal to the poling direction[22].

The fact that there exists a threshold value of electric field indicates that the residual stresses in PZT-5H play an important role in non-180$^o$ domain switching and phase change. In depolarized samples, residual stresses are relatively uniformly distributed throughout the material. Therefore, the threshold energy for domain switching and phase change in different grains is similar. Once such threshold energy level is reached upon an applied electric field, non-180$^o$ domain switching and phase transition occur. In a polarized sample, however, residual stress level differs profoundly from grain to grain and so is the threshold energy. Therefore, non-180$^o$ domain switching and phase transition in different grains/domains may be induced at different applied electric field levels, resulting in a continuous change in nonlinear piezoelectric constants[15,16].

Figure 5 shows pseudo–cubic (111) and (220) peaks in polarized samples. Under positive field, the magnitudes of the change are very small. However, the changes under negative electric fields are rather large. The nonlinear behavior of piezoelectric effects is found to depend on the direction of the applied electric field[18]. The strong direction-dependent peak profile changes shown in Figs. 4 and 5 are responsible for this nonlinear behavior. Moreover, it is interesting to find that around negative coercive field (-0.8$E_C$), a large profile change is induced by the electric field. The change corresponds to a large piezoelectric contraction and can explain the deep minima found in the strain-electric field hysteresis loop[16,28]. It is commonly believed that a negative electric field induces 180$^o$ domain switching. However, our results in Fig.5 showed that, with magnitude below the coercive field, a negative electric field induces a large amount of non-180$^o$ domain

switching. This effect is likely due to the residual stresses generated during the poling process.

### 3.2 Fitting of Peaks

Because of the co-existence of morphotropic phases, each of the above pseudo-cubic diffraction peaks is composed of multiple peaks corresponding to different phases. Table 1 lists all the possible peaks at pseudo-cubic (111), (200), and (220) regions for tetragonal, rhombohedral and monoclinic phases in PZT-5H. In principle, all these phases, therefore the corresponding peaks, may be present in the material and thus within a particular pseudo-cubic peak. To study possible domain switching and phase transition, we conducted peak fitting to determine the individual peaks for different phases. We focused on the pseudo-cubic (111), (200), and (220) regions since other peaks would either contain too many individual peaks for different phases or have too low a $2\theta$ angle to be very accurate.

We consider a mixture of two phases, either a mixture of tetragonal and rhombohedral phases or that of tetragonal and monoclinic phases. Practically, the number of individual peaks would be too large if we tried to fit the peaks to a mixture of three phases. Two methods are used in the fitting: one is to fit the individual peaks of the two phases to each of the three experimentally measured pseudo-cubic peaks; the other is to fit the individual peaks of the two phases to pseudo-cubic (220) peak to determine the lattice parameters of the two phases, and then use the lattice parameters to calculate the $2\theta$ values of other peaks in the two phase mixture at pseudo-cubic (111) and (200) regions.

As seen in Table 1, for the pseudo-cubic (111), (200), and (220) peaks, we need to fit 3, 3, and 4 individual peaks for a mixture of tetragonal and rhombohedral phases; or 4, 4, and 6 peaks for a mixture of tetragonal and monoclinic phases, respectively. The fitted 2θ values of individual peaks are listed in the third column in Table 2, where T, R, and M stand for tetragonal, rhombohedral, and monoclinic phases.

With the second method mentioned above, by using the pseudo-cubic (220) peak, we minimized the low angle distortion effect. Moreover, there are enough peaks to determine all lattice parameters. The lattice parameters for a mixture of tetragonal and rhombohedral phases are determined as, tetragonal: $a$ = 4.0596Å, $c$ = 4.1158Å, Rhombohedral: $a$ = 4.0857Å, $\alpha$ = 89.668°; and those for a mixture of tetragonal and monoclinic phases, tetragonal: $a$ = 4.0595Å, $c$ = 4.1140Å, Monoclinic: $a_m$ = 5.7920Å, $b_m$ = 5.7541Å, $c_m$ = 4.0989Å, $\beta$ = 90.443°. The calculated peak positions at pseudo-cubic (111) and (200) directions using these lattice parameters are given in the second column in Table 2. It is clearly seen in Table 2 that the peaks positions obtained by these two methods agree with each other extremely well, rendering confidence in the current peak fitting methods and in the accuracy of the determined lattice parameters.

The results in Table 2 seem to suggest that both morphotropic phase compositions, i.e., mixture of tetragonal and rhombohedral phases or mixture of tetragonal and monoclinic phases, are possible compositions at room temperature. The current method is not able to determine which of these is the more likely microstructure of PZT-5H.

### 3.3 Effects of Electric Fields on Domain Switching and Phase Change

With the information on individual peak positions and intensities of different phases, we are now able to study the domain switching and phase change induced by the applied electric field. Figure 6 illustrates the fitted peaks at pseudo-cubic (200) region in a depolarized sample at $E = 0$ and $E = E_C$. Figure 6(a) shows the fitted peaks for a mixture of tetragonal and rhombohedral phases. It clearly shows that, as an electric field of $E_C$ is applied, the intensity of T(002) increases while that of T(200) decreases, indicating 90° domain switching of tetragonal phase from the (200) to the (002) orientation. Moreover, the intensity of R(200) is decreased upon applied electric field, indicating a phase transition from rhombohedral to tetragonal, R(200) to T(002). Similar phenomenon is observed in Fig. 6(b) for a mixture of tetragonal and monoclinic phases. Upon applied electric field of $E_C$, there is a clear indication of 90° domain switching of the tetragonal phase from (200) to (002) orientation, and a phase change from M(220) to T(002). However, the intensity of the peak M(002) remains nearly the same upon applied electric field, indicating that this orientation is still the preferred one for the monoclinic phase upon applied electric field.

Results for the pseudo-cubic (200) peak of a polarized sample are given in Fig. 7. Figure 7(a) shows fitted peaks for a mixture of tetragonal and rhombohedral phases at 0, $E_C$, and $-0.8E_C$. The changes of the peak intensities indicate that, upon an applied electric field of $E_C$, 90° domain switching from T(200) to T(002) and phase transition from R(200) to T(002) are induced, but only in a very small amount. On the other hand, upon an electric field of $-0.8E_C$, 90° domain switching from T(002) to T(200) and phase transition from T(002) to R(200) are clearly induced in a large amount. Figure 7(b) shows

fitted peaks for a mixture of tetragonal and monoclinic phases at 0, $E_C$, and -0.8$E_C$. Upon an electric field of $E_C$, similar domain switching and phase transition behaviors as those observed in Fig. 6(b) are also induced in a polarized sample, but in a very small amount. Whereas upon an electric field of -0.8$E_C$, domain switching and phase transition in the opposite direction to those in Fig. 6(b) are induced in a large amount.

## IV. CONCLUSIONS

Electric field induced domain switching and phase transition were studied using *in-situ* x-ray diffraction. Through the changes of x-ray diffraction profiles of pseudo-cubic peaks upon applied electric field, we identified when the switching and transition occur. Our results indicate that, for a depolarized PZT-5H sample, there exists a threshold field level below which little non-180° domain switching or phase transition occurs. This threshold value is significantly lower than the material's coercive field. In a polarized sample, on the other hand, no obvious threshold exists. When the applied electric field is in the same direction as the poling direction, the non-180° domain switching and phase change occur from a low electric field, although the switching and transition happen rather slowly as the applied electric field level increases. When the applied electric field is in the opposite direction from the poling direction, however, the changes are much more profound. These observations indicate that residual stresses in the material play an important role in inducing domain switching and phase change. The dependence of the non-180° domain switching and phase transition on the applied electric field in polarized materials is believed to be responsible for the electric field direction-dependent nonlinear piezoelectric behavior of PZT-5H.

Furthermore, by fitting the individual peaks of tetragonal, rhombohedral, and/or monoclinic phases to the measured pseudo-cubic (111), (200), and (220) peaks, we established that the material may be composed of a mixture of tetragonal and rhmbohedral phases or a mixture of tetragonal and monoclinic phases. The peak fitting method also allows us to identify the electric field induced $90^o$ domain switching in the tetragonal phase as well as the phase transitions between the tetragonal and rhombohedral phases or between the tetragonal and monoclinic phases.

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Table 1. Peaks at pseudo−cubic (111), (200), and (220) regions

| Pseudo−cubic | (111) | (200) | (220) |
|---|---|---|---|
| Tetragonal | (111) | (002), (200) | (202), (220) |
| Rhombohedral | (111), $(\bar{1}11)$ | (200) | (220), $(\bar{2}20)$ |
| Monoclinic | $(\bar{2}01)$, (021), (201) | (002), (220) | $(\bar{2}22)$, (222), (400), (040) |

Table 2. Fitted and computed peaks at pseudo–cubic (111), (200), and (220) regions

(Wavelength $K\alpha_1$: 1.5406 Å)

| Tetragonal and Rhombohedral | | | Tetragonal and Monoclinic | | |
|---|---|---|---|---|---|
| Peak | Computed $2\theta$ ($^o$) | Fitted $2\theta$ ($^o$) | Peak | Computed $2\theta$ ($^o$) | Fitted $2\theta$ ($^o$) |
| R(111) | 37.892 | 37.936 | M($\bar{2}$01) | 37.871 | 37.936 |
| T(111) | 38.194 | 38.114 | M(201) | 38.158 | 38.114 |
| R(1$\bar{1}$1) | 38.197 | 38.114 | M(021) | 38.187 | 38.114 |
| T(002) | 43.964 | 43.967 | T(111) | 38.200 | 38.114 |
| R(020) | 44.306 | 44.271 | T(002) | 43.984 | 43.920 |
| T(200) | 44.605 | 44.516 | M(002) | 44.156 | 44.129 |
| R(220)* | 64.246 | 64.246 | M(220) | 44.347 | 44.362 |
| T(202)* | 64.422 | 64.422 | T(200) | 44.606 | 44.539 |
| R($\bar{2}$20)* | 64.662 | 64.662 | M($\bar{2}$22)* | 64.172 | 64.172 |
| T(220)* | 64.917 | 64.917 | M(400)* | 64.280 | 64.280 |
| | | | T(202)* | 64.438 | 64.438 |
| | | | M(222)* | 64.565 | 64.565 |
| | | | M(040)* | 64.753 | 64.753 |
| | | | T(220)* | 64.919 | 64.919 |
| Lattice Parameters: Tetragonal: $a$ = 4.0596Å, $c$ = 4.1158Å; Rhombohedral: $a$ = 4.0857Å, $\alpha$ = 89.668$^o$ | | | Lattice Parameters: Tetragonal: $a$ = 4.0595Å, $c$ = 4.1140Å; Monoclinic: $a_m$ = 5.7920Å, $b_m$ = 5.7541Å, $c_m$ = 4.0989Å, $\beta$ = 90.443$^o$ | | |

* Peaks used to calculated lattice parameters

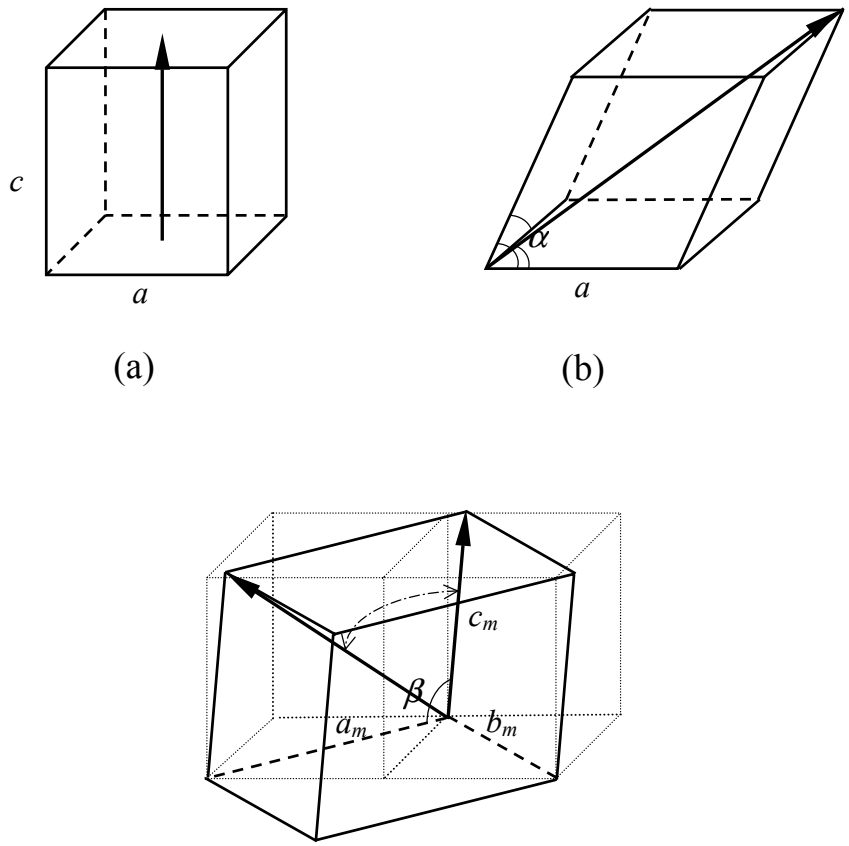



Fig. 1 Unit cells of individual phases in PZT: (a) tetragonal, (b) rhombohedral, (c) monoclinic.

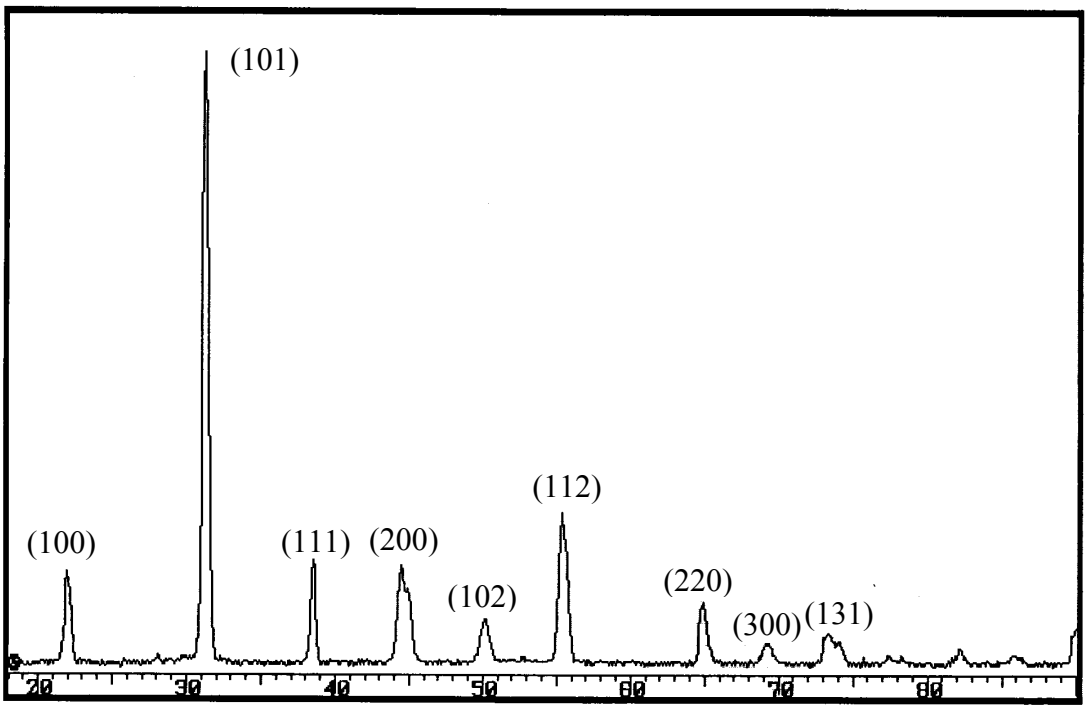



Fig. 2 Diffraction profile of a polarized sample.

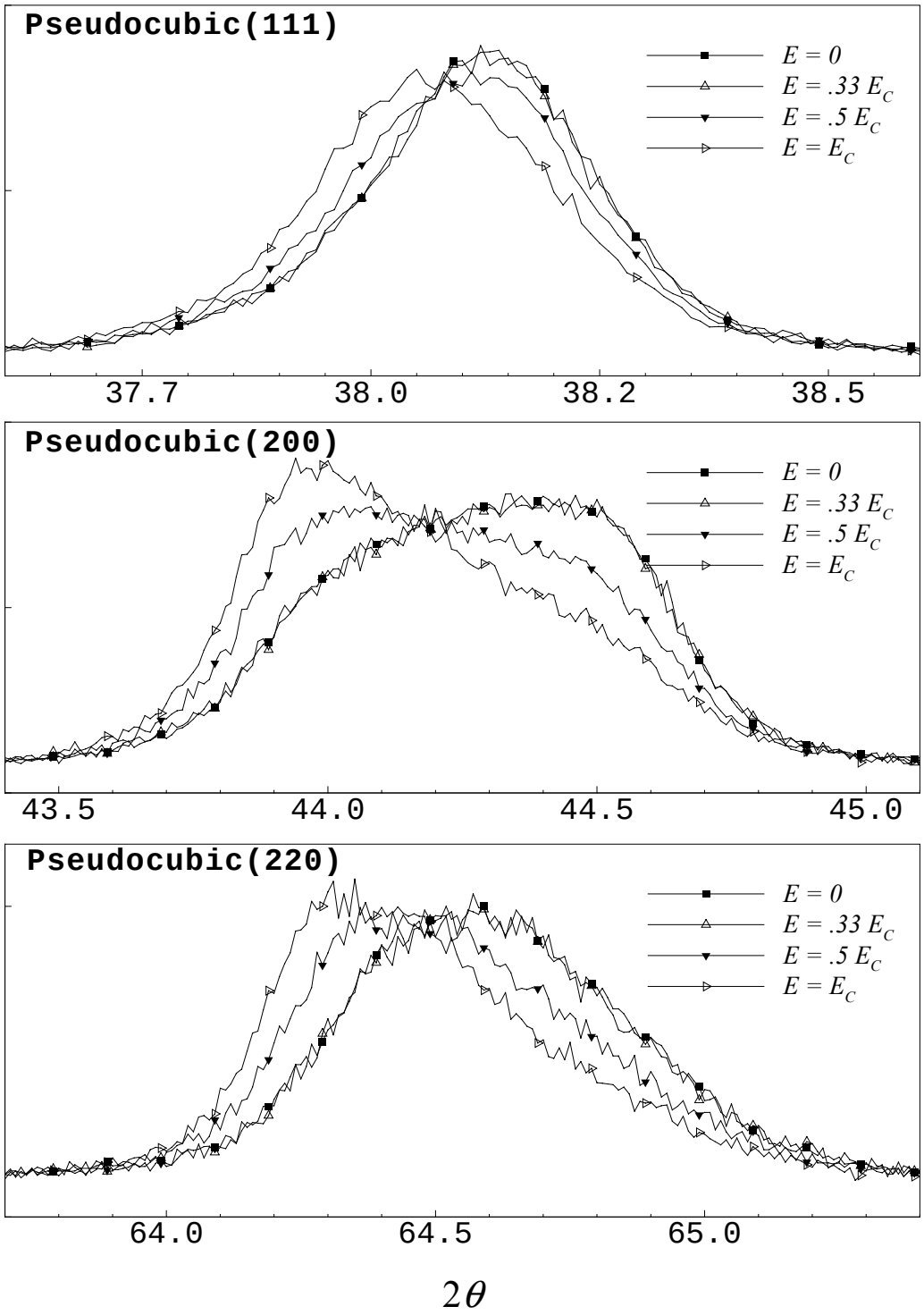



Fig. 3 Pseudo–cubic peaks of a depolarized sample under several positive electric field levels: (a) (111) peak, (b) (200) peak, (c) (220) peak.

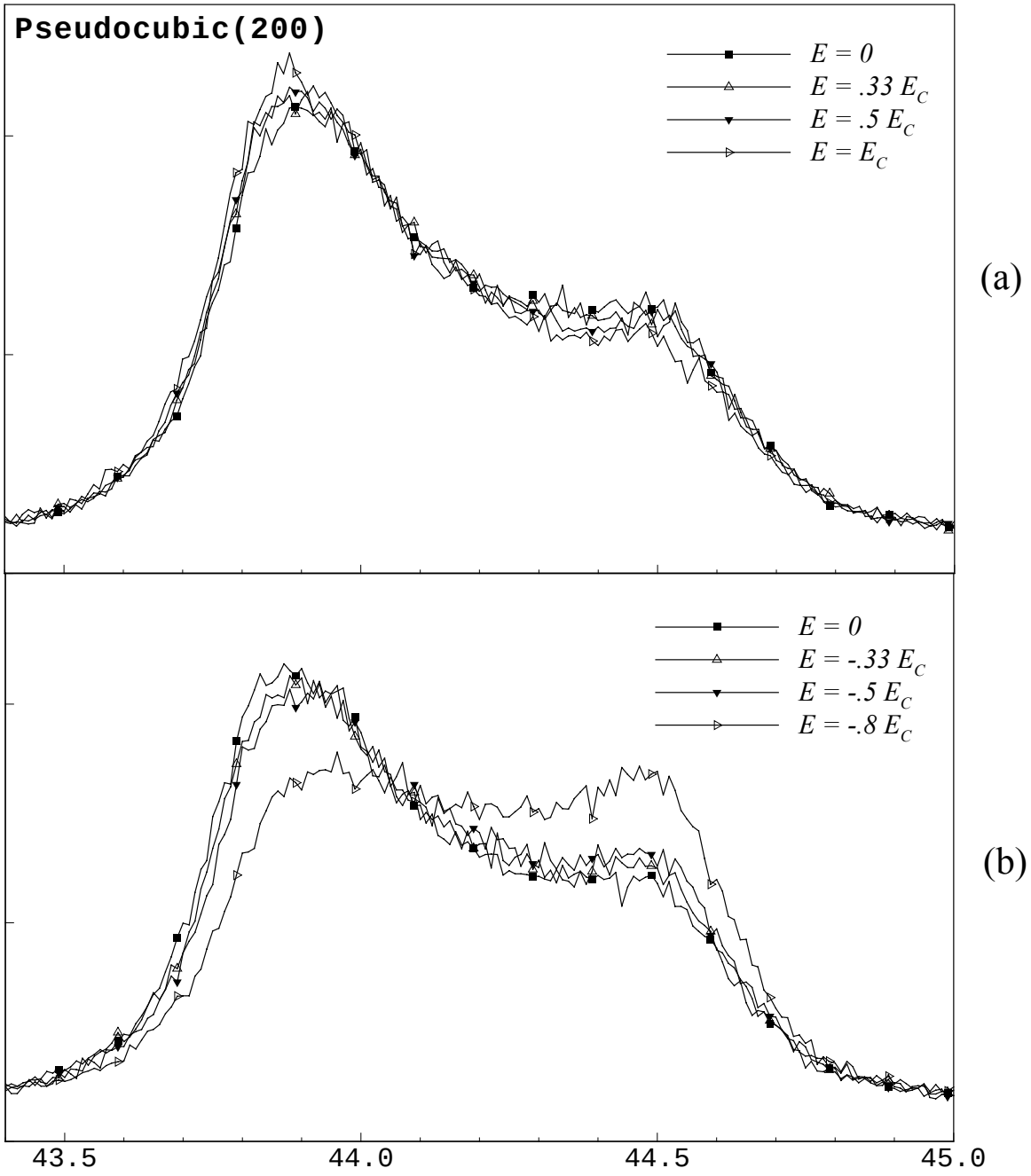



Fig. 4 Pseudo−cubic (200) peak of a polarized sample: (a) under different positive electric field levels, (b) under different negative electric field levels.

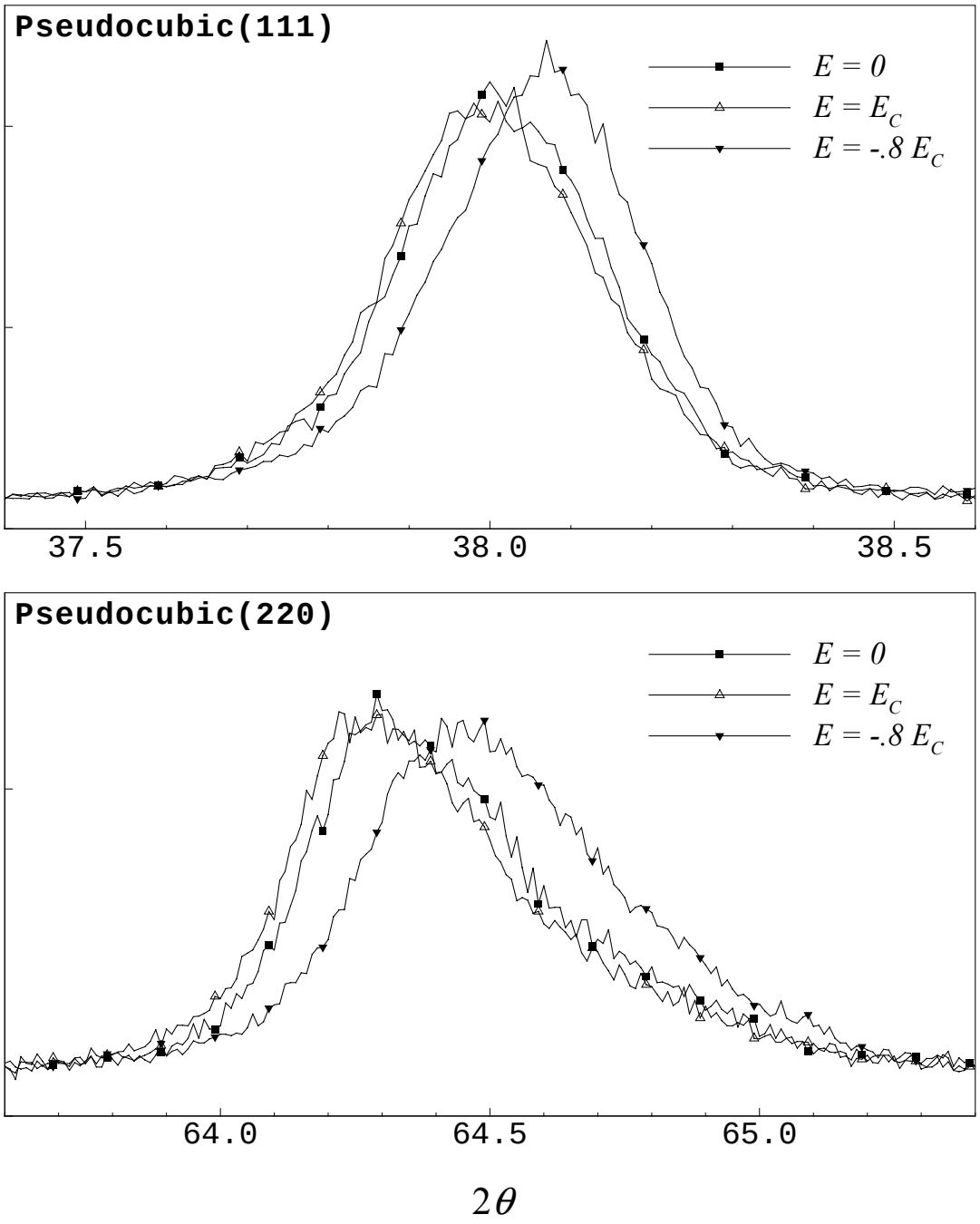
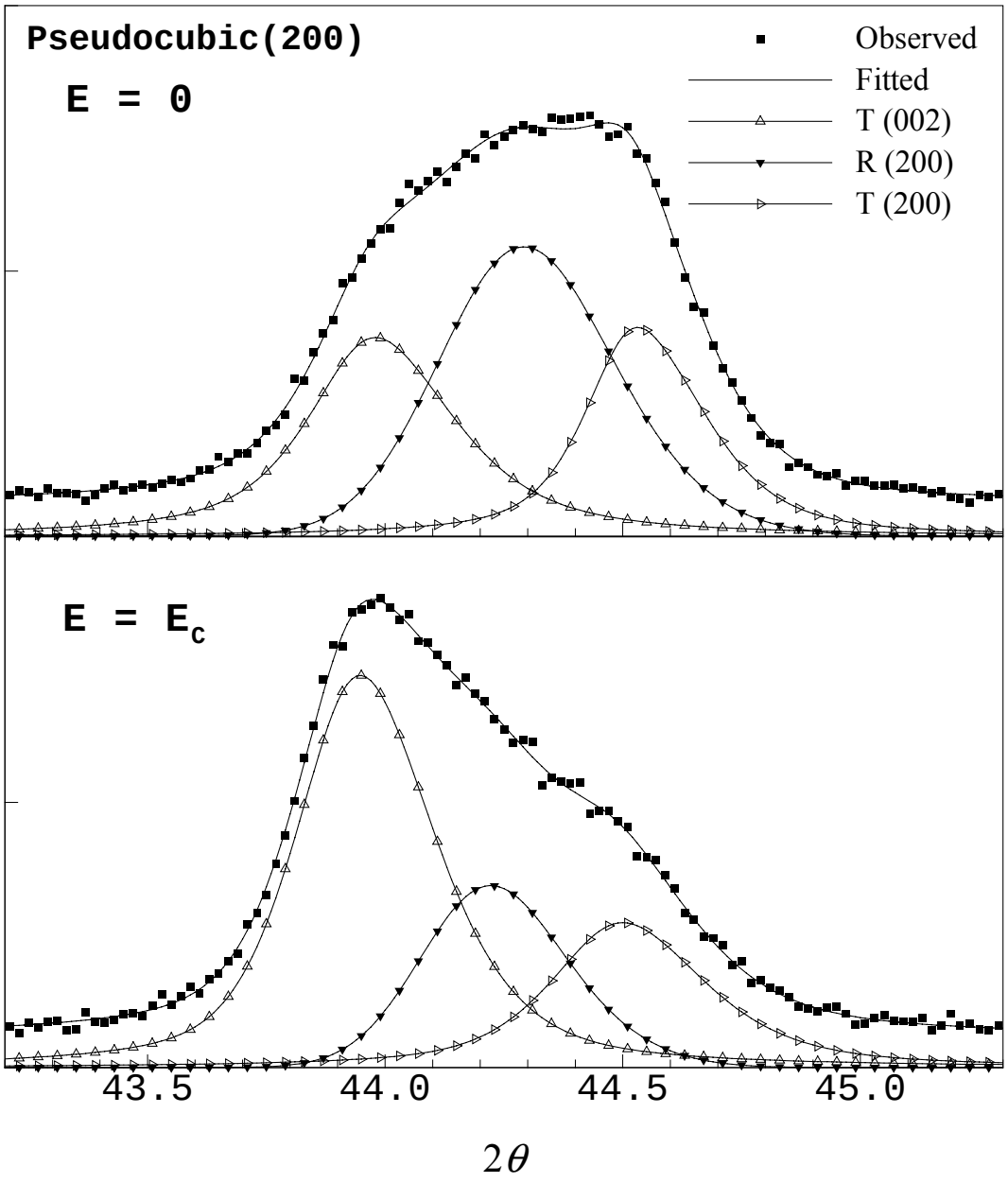
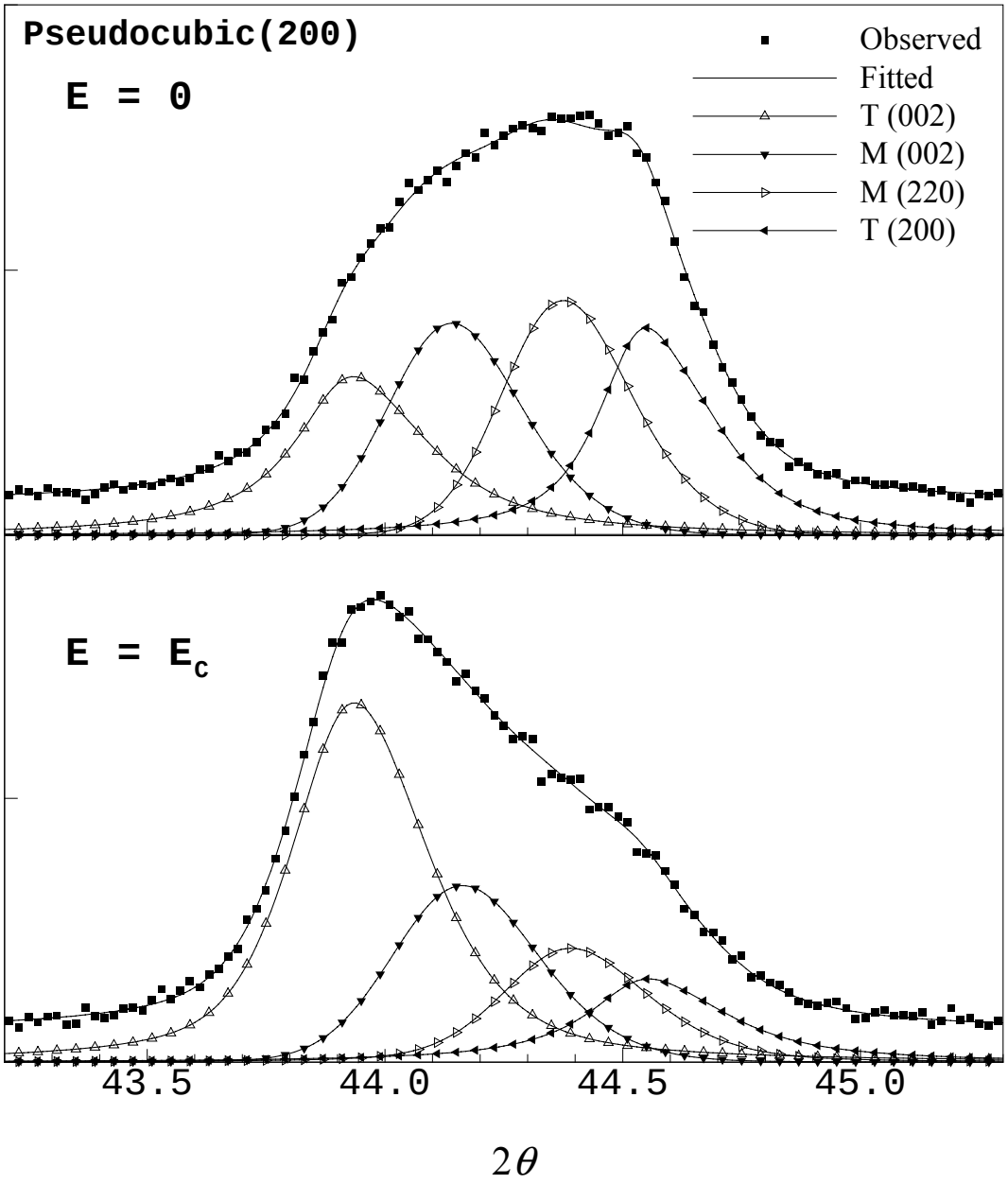



Fig. 5 Pseudo−cubic (111) and (220) peaks of a polarized sample under zero, a positive, and a negative electric fields: (a) (111) peak, (b) (220) peak.



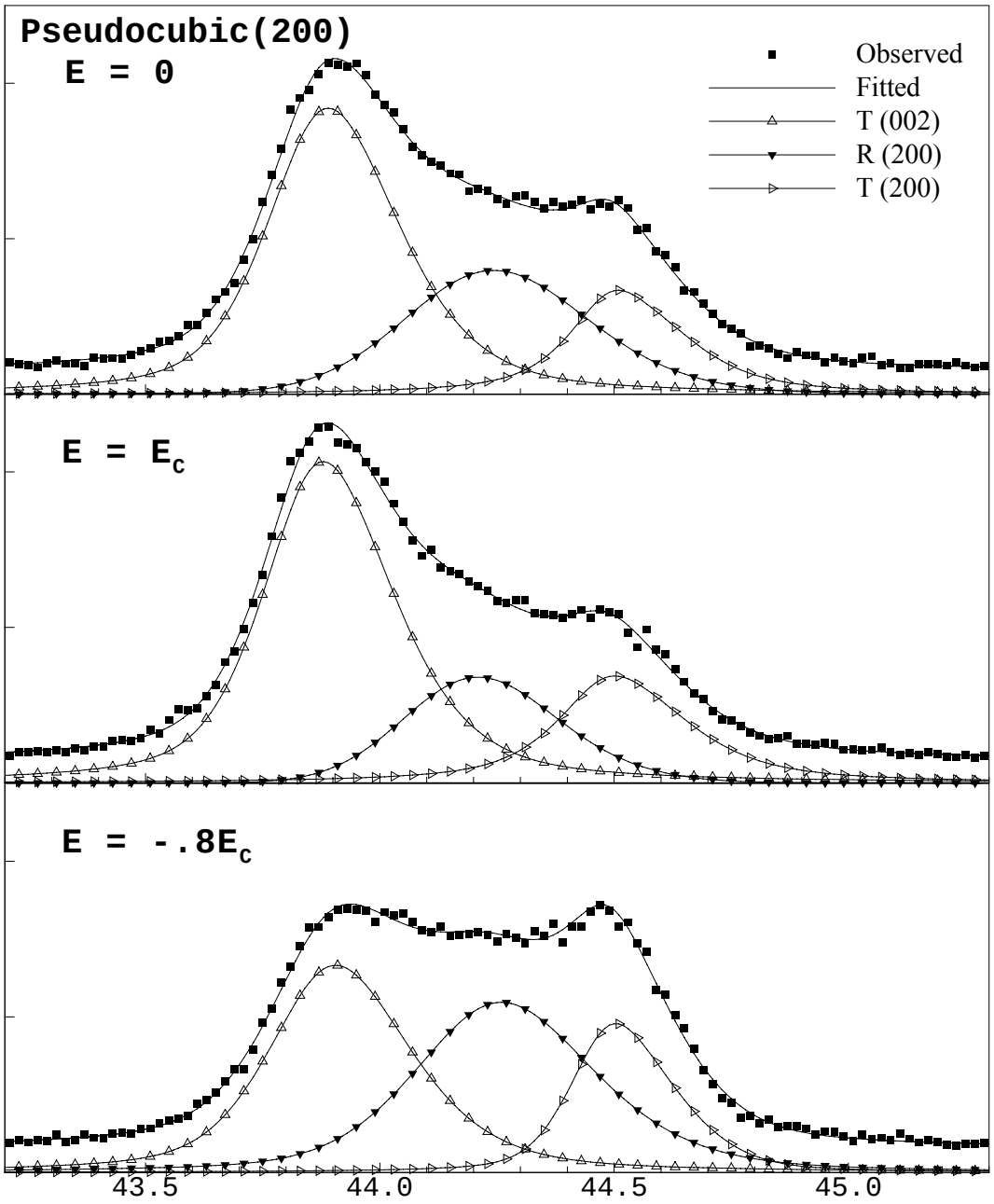

(a)

Fig. 6 Fitted peaks at pseudo−cubic (200) region of a depolarized sample: (a) mixture of tetragonal and rhombohedral phases



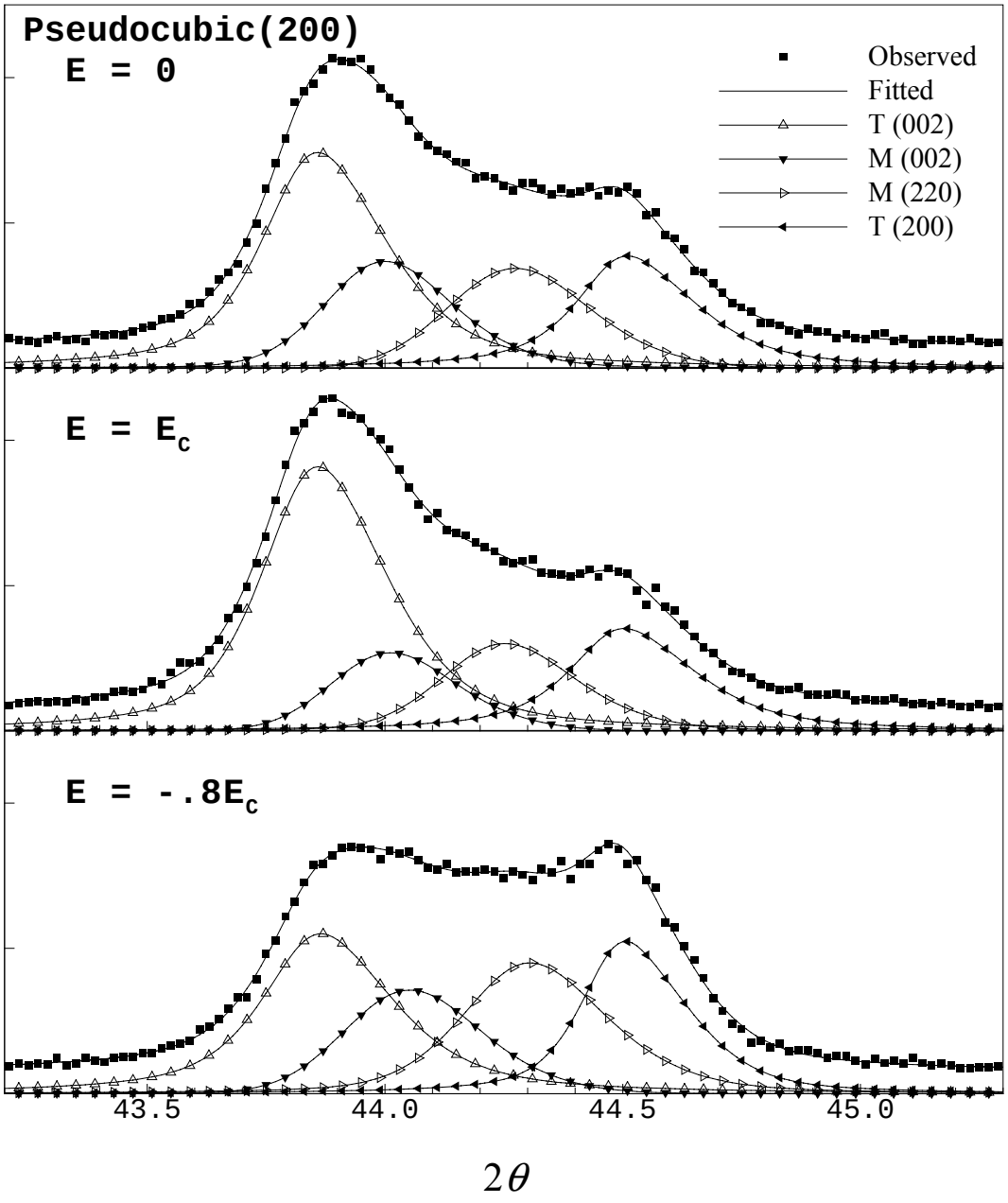

(b)

Fig. 6 (Cont'd) Fitted peaks at pseudo–cubic (200) region of a depolarized sample: (b) mixture of tetragonal and monoclinic phases.




(a)

Fig. 7 Fitted peaks at pseudo–cubic (200) region of a polarized Sample: (a) mixture of tetragonal and rhombohedral phases




(b)

Fig. 7 (Cont'd) Fitted peaks at pseudo−cubic (200) region of a polarized Sample: (b) mixture of tetragonal and monoclinic phases.

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