Surface potential of BaTiO$_3$ single crystal near the Curie temperature

L. Makhova, R. Hesse, M. Ullrich, and R. Denecke

Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie Universität Leipzig,
Linnéstraße 2, D-04103 Leipzig, Germany

I. Konovalov

FH Jena, Carl-Zeiss-Promenade 2, D-07745 Jena, Germany

A shift in the binding energies in Ba $3d$ and Ti $2p$ core-level spectra was observed when the electronic properties of nonprepolarized and prepolarized BaTiO$_3$ surfaces were studied using x-ray photoelectron spectroscopy during heating and cooling near the Curie temperature (T_C). From a comparison of this shift for nonprepolarized and prepolarized crystals, different magnitudes and directions were noted. The differences are not connected with chemical shifts induced by any new chemical bonds. The shift in binding energy is considered to be a change of surface potential due to surface charging caused by the heating of the ferroelectric crystal through T_C.

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I. INTRODUCTION

Due to increasing interest in multiferroic materials with coupled magnetic and electric polarizations,[1–4] BaTiO$_3$ remains to be studied in detail as a suitable ferroelectric component.

A ferroelectric structure combined with a transparent semiconductor, such as ZnO, would also be attractive as a base material for heterostructures with the potential for controlling the polarization orientation with an applied electrical bias.[5,6] The ferroelectric state is known to be very sensitive to surface effects.[7] In addition, the properties of ferroelectrics, for example, the dielectric permittivity, polarization, and domain formation, strongly depend on the temperature. The influence of the varied parameters and properties of samples on the surface potential determined by x-ray photoelectron spectroscopy (XPS), especially in the temperature range about the Curie temperature (T_C), has not been described thus far.

Despite the widespread application of BaTiO$_3$, there are many open questions about its ferroelectricity, such as the primary driving force for the transitions[8] and n type of conductivity between room temperature and 100 °C.[9] For optical applications of BaTiO$_3$, it is necessary to know the relationship between the domain structure on its surface and its dielectric properties.[10,11] For example, the presence of domain regions, usually 180° domains, can increase the dielectric constant of BaTiO$_3$.[10,12] The polarization direction of the domains can be changed by using an external electric field at a temperature lower than T_C (tetragonal phase). The domain structure can be observed by scanning probe microscopy. The surface potential of a multidomain BaTiO$_3$ surface can be imaged both in the presence and absence of ultraviolet (UV) illumination.[13] Another surface-sensitive method, such as XPS, allows the investigation of the change in surface potential (i.e., the shift in binding energy E_B). Only a few papers present XPS studies of a BaTiO$_3$ surface, but these studies are devoted to investigating the electronic structure, the character of the chemical bonding, and a comparison of spectra of the structures prepared and cleaned by different methods (e.g., sputtering, annealing *ex situ* and *in situ*).[14–18] From these investigations, it is well known that high-temperature annealing creates new surface phases and that subsequent heating in a vacuum produces an n-type material through the formation of O vacancies.[19,20] It is important to use nonreduced BaTiO$_3$ crystals to study the surface-potential change, thereby preventing charge migration.

The aim of this study was to investigate the change in the surface potential for BaTiO$_3$ single crystals during the phase transition by taking measurements through the Curie temperature. To avoid the formation of any defects at the surface and in the bulk of the sample, the crystal was not annealed at a high temperature. Prior to the measurement, the sputtering process, which produces nonstoichiometric surface selvage,[19] was not performed either. XPS was used to investigate the surface potential of BaTiO$_3$ and its change during the heating of the crystal through the T_C. The temperature dependence of the binding energy of Ba $3d_{5/2}$ and Ti $2p_{3/2}$ core electrons was studied. Measurements were performed on randomly polarized BaTiO$_3$ single crystals and crystals polarized deliberately by external electric field.

II. EXPERIMENTAL DETAILS AND TECHNIQUES

BaTiO$_3$ (100) single crystals were purchased from CrysTec. The orientation accuracy for these crystals was better than 2°.

The investigation of the BaTiO$_3$ crystal surface was performed by XPS (the information depth is ∼2 nm). The photoelectron spectra were recorded with a VG ESCALAB 220iXL spectrometer using nonmonochromatized Mg K_α radiation with an energy of 1253.6 eV. For the measurements of the dependence of binding energy on temperature, a recording software called "AVANTAGE" was used. This program permits the varying of the time and the number of scans for the measurement of separate peaks. Each scan is presented as a separate measured photoelectron count rate (I_e) vs E_B in the correspondent temperature range. The fit procedure of peaks and the presentation of the experimental results as three-dimensional (3D) color profiles were performed using UNIFIT software package.[21,22] Peak fits were carried out by convolution of Lorentzian and Gaussian functions. The determination of the peak positions and intensities proceeded iteratively by a nonlinear parameter-fitting routine.

The background parameters were fitted parallel to the peak fit with constant and Tougaard components.[21]

For investigation of the temperature influence on the binding energy of Ti $2p$ or Ba $3d$ core levels, the single crystal was annealed at 250 °C for 5 min in a vacuum (typically 10^{-9}–10^{-10} mbar) and quickly transferred *in situ* to the XPS analysis chamber. In the second experimental series, heating followed by cooling of the crystal was performed in the analysis chamber during continuous measurements of the photoelectron spectra. The sample temperature during cooling was determined by using a calibration graph of the temperature vs time that was obtained in the preparation chamber. The determination of the temperature from this calibration graph during the XPS measurement was accurate to within ± 10 °C and was confirmed by the appearance of visible domains at T_C. The Curie temperature was detected using optical equipment (a zoomed image taken by a video camera). During heating the T_C was detected through visual observation of the disappearance of the domains in BaTiO₃.

For comparison, the same single crystal BaTiO₃ was also annealed at a temperature of 700 °C. This is in contrast to the usual experiments which were carried out at a temperature not exceeding 250 °C to avoid defect formation, as previously noted.

The electrical prepolarization of BaTiO₃ was carried out *ex situ* using an external electric field. During prepolarization a negative voltage of 1 kV was applied to a metallic foil pressed against the polished surface of the crystal on which the subsequent photoelectron measurements were performed (on the front side). In the other experiments, the same voltage was applied to the surface of the crystal opposite to where XPS measurements were performed. In both cases the sample was fixed to a metallic base where the positive pole of the voltage supply was connected. The prepolarization process was carried out at 90 °C for 10 h in air. Then the sample was cooled to room temperature, and the voltage supply was switched off. Heating was carried out slowly to avoid large mechanical stress in the volume of the crystal.

The influence of a possible piezoelectric effect accompanying the ferroelectricity was investigated. For these experiments, a special holder, which induced the mechanical stress in the different directions of the sample, was used. No influence of the piezoelectric effect on the core-level shift in XPS measurements was observed.

III. RESULTS

Prior to the investigation of surface properties, the surface of the BaTiO₃ single crystal was cleaned by heating at 250 °C for 5 min in the preparation chamber attached to the ESCALAB spectrometer. During continuous recording of Ba $3d$ and Ti $2p$ core-level spectra while the crystal was cooling in the analysis chamber, a large sudden shift in binding energies in the spectra of both elements was observed. This shift, a so-called "jump," appeared at about 120°C, which is the Curie temperature of BaTiO₃ according to the literature. Figure 1
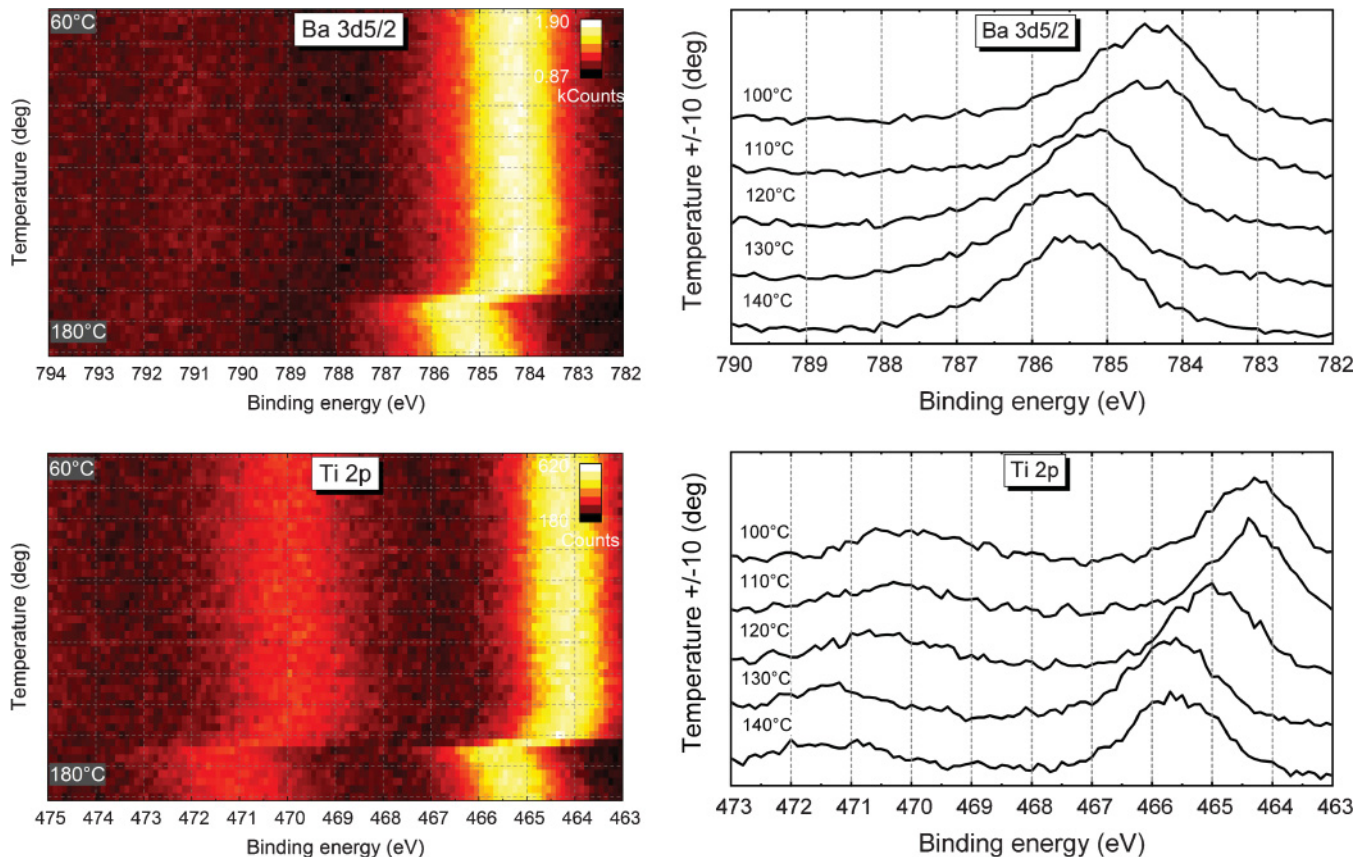

FIG. 1. (Color online) Ti $2p$ and Ba $3d_{5/2}$ photoelectron spectra vs temperature during the cooling process (the graphs placed to the right of figure present only selected scans recorded near T_C).
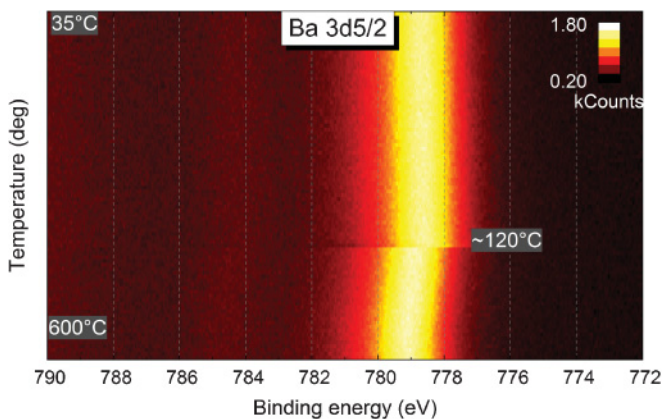
FIG. 2. (Color online) Ba $3d_{5/2}$ photoelectron spectra vs temperature during cooling after high-temperature annealing at 700 °C.

presents the change and the jump in binding energies for the Ba $3d_{5/2}$ and Ti $2p_{3/2}$ core-level spectra. Cooling of the sample was carried out from ∼180 to ∼60°C (above and below the Curie temperature). The presentation of measurement results as 3D color profiles using the UNIFIT program[22] (to the left of Fig. 1) permits the visualization of the jump in energy more effectively.

Because the jump in energy takes place at about 120°C (the Curie temperature of BaTiO₃), this effect is directly connected with the phase transition and the change in ferroelectric behavior of BaTiO₃. No additional spectral components were observed in the Ba $3d_{5/2}$ and Ti $2p$ core-level spectra (Fig. 1): therefore this shift is not a chemical shift connected with the formation of new chemical bonds. It should be noted that the binding energies of core levels are always larger than, for example, the values published by other researchers [E_B (Ba $3d_{5/2}$) = 779.6 eV and E_B (Ti $2p_{3/2}$) = 459.0 eV].[19,20] However, these literature values are presented for BaTiO₃ samples annealed at a high temperature. In comparison to the results obtained for the nonannealed crystals, the surface of the samples used in this study was positively charged. A reference

measurement of a sample annealed at 700°C was carried out (Fig. 2). The binding energy of Ba $3d_{5/2}$ was about 779.2 eV and a smaller jump was observed near the Curie temperature. Annealing of BaTiO₃ at a high temperature in a vacuum is known to change the conductive properties of BaTiO₃ due to the formation of oxygen vacancies and to change the surface reconstruction.[23,24]

The following experiments show that the jump effect takes place during heating as well. These experiments were carried out in the analysis chamber in which photoelectron spectra were recorded during the heating and during the subsequent cooling of the sample. Figure 3 (the black and white images in the middle of the figure) demonstrates the presence of domains in BaTiO₃ at a temperature below 120°C and their disappearance at a temperature above 120°C. A notable jump in the binding energy was observed at the time of domain disappearance during heating; therefore the energy shift happens at T_C. While the jump in the energy during cooling was about 2 eV, the jump during heating was larger; in fact, the value of the binding energy exceeded the measurement range (i.e., 779–793 eV, Fig. 3).

The behavior of the surface potential after prepolarization of the sample was investigated to verify whether the jump depends on the polarization direction. Figure 4 presents the spectra during heating of the crystal with various directions of prepolarization. All spectra show the jumps in the binding energies during heating, however, the direction of the jumps is different. During cooling, the jump direction was always towards smaller binding energies for all samples (Fig. 1). The change in the direction of the jump takes place only during heating of prepolarized samples. Additionally, the movement of the domains was visually observed during heating at temperatures below T_C. This movement was accompanied by random shifts in the surface potential [Fig. 4(b)]. These shifts are exactly the same for Ba $3d_{5/2}$ and Ti $2p$ core-level spectra measured almost simultaneously. The peak shape analysis[21] of both core-level photoelectron spectra also confirmed the absence of additional components in the spectra of the BaTiO₃ surface recorded at all other times and temperatures. Therefore
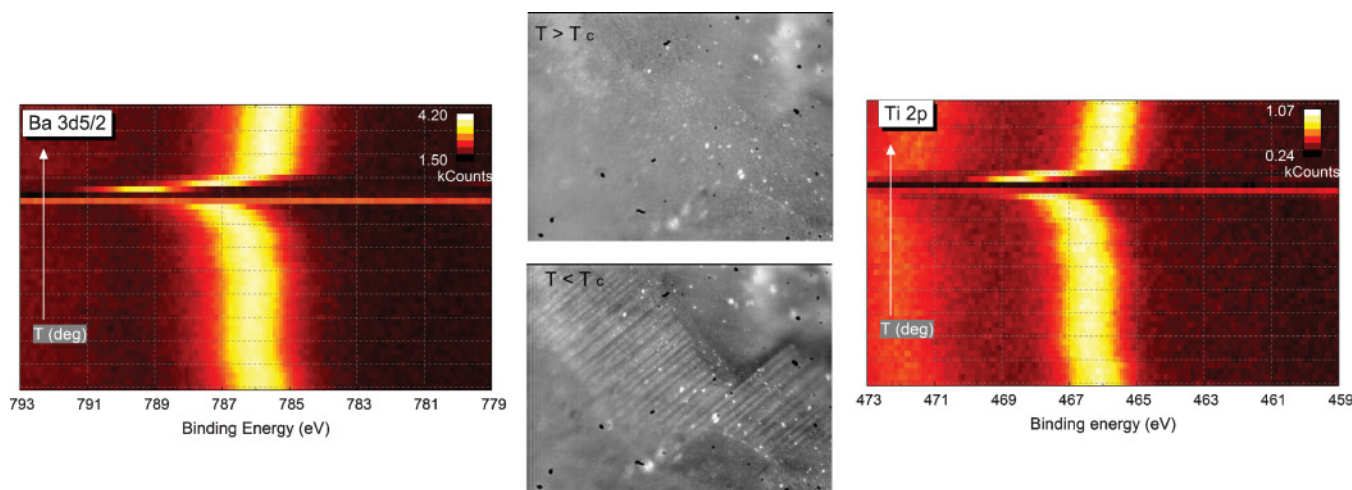

FIG. 3. (Color online) Ba $3d_{5/2}$ and Ti $2p$ photoelectron spectra vs the scan number recorded during heating (temperature increases from bottom to top). The jump in the binding energies in the range of T_C during heating. At temperatures above T_C the ferroelectric domains disappear–optical images are in the center.
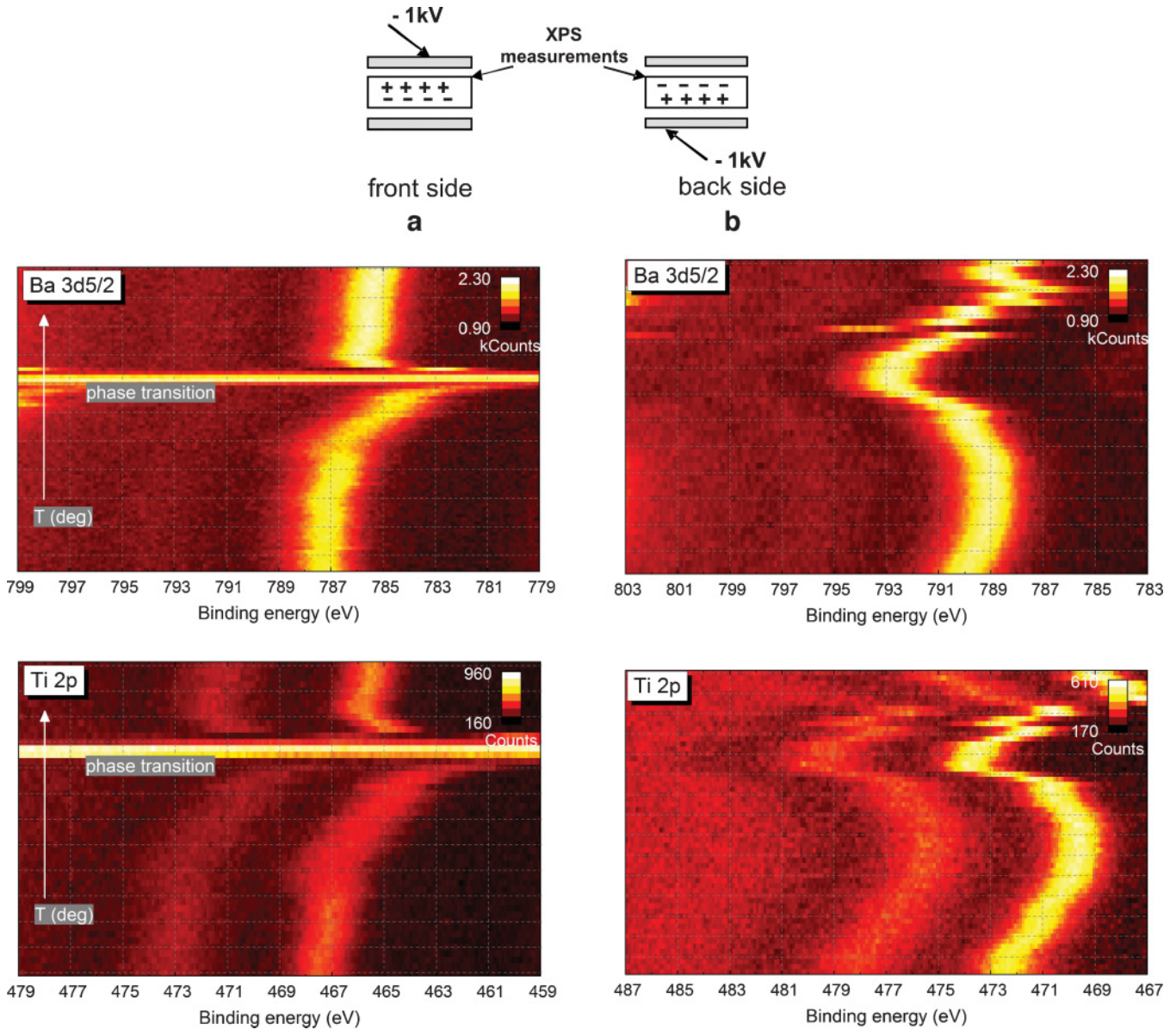
FIG. 4. (Color online) Ba $3d_{5/2}$ and Ti $2p$ photoelectron spectra vs the scan number recorded during heating (temperature increases from bottom to top) for samples: (a) after prepolarization from the front side and (b) after prepolarization from the back side.

the shift in binding energy cannot be due to a chemical shift caused by new chemical bonds or structures.

IV. DISCUSSION

To our knowledge, the jump in binding energies discovered in these XPS experiments has not been previously reported in the literature. This behavior of the surface potential is difficult to interpret in detail. A striking feature of many of the spectra is a strong deviation of the count rate of the whole spectrum during the phase transition. This deviation is visible as a bright line in Fig. 4(a). The origin of additional photoelectrons in such large quantities is not easily explained. High count rates in wide spectral regions are typical for regions of the spectra with small kinetic energy caused by scattered electrons (Fig. 5). The bright lines in the spectra of Fig. 4(a) can thus be explained by assuming a shift of all the spectral features due to a sudden

charging of the surface by several tens of volts. Figure 5 illustrates how the region of the high count rate of scattered electrons moves into the measurement window during a large negative charging of the surface. Dark lines visible in Fig. 3 with count rates smaller than the background can be explained in a similar way. According to this interpretation, the jump in Fig. 4(a) is due to the lower binding energies for the frontal polarization direction with the negative electrode at the measured surface.

It is apparent that the change in the binding energy is caused in part by the surface charging due to photoelectrons. There are several other possible factors that could influence the surface potential and the energy shift, such as the sample resistivity and the dielectric permittivity. A few papers report a sudden change in the resistivity at the transition temperature.[24–26] However, these observations are related to either extrinsically doped semiconducting $BaTiO_3$ or to polycrystalline $BaTiO_3$, in which
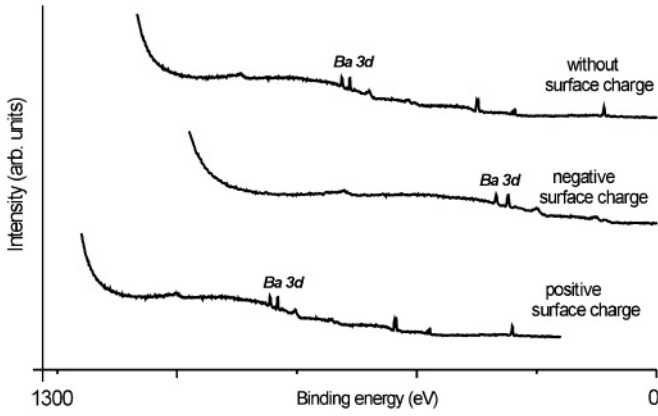
FIG. 5. Schematic for the interpretation of bright and dark lines in Figs. 3 and 4 by a shift in the peaks along the E_B axis in the photoelectron spectrum because of different surface charging.

the high resistance is caused by grain boundaries. These data suggest the possibility of a large resistivity jump in BaTiO₃. For a single crystal, no changes of the resistivity were reported near the Curie point.[25]

Another possibility is that the jump is a result of a change in the dielectric permittivity ε. In the existing microscopic regions with the same dipole orientation, domains of spontaneous polarization (see Fig. 3), ε changes with a change in temperature.[26] The maximal ε value is reached at the Curie point, and after the phase transition (transformation of the tetragonal lattice to the cubic one) and the disappearance of the domains, this value decreases according to the Curie-Weiss law[27,28] (Fig. 6). Indeed, the size of the jump during heating in these measurements is larger than that during cooling (Fig. 3) therefore the potential changes are similar to the change of ε in Fig. 6. However, if the strong change in the binding energy of the core levels is only due to the behavior of ε, the polarization of the sample by an external electrical field applied to the front and back sides of the sample should not influence the direction of the jump in the binding energy.
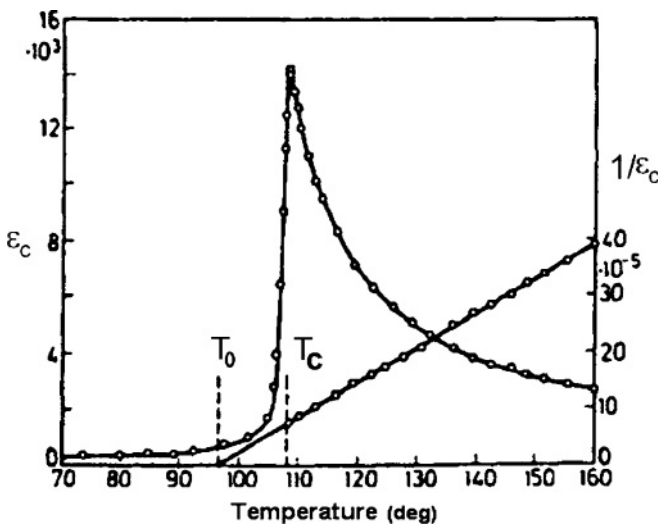

FIG. 6. Dependence of ε_C and $1/\varepsilon_C$ on temperature near the phase transition (Ref. 27).

The change in the electrical potential at a depth of 1–2 nm during the phase transition, in the region where most of the photoelectrons originate, is determined by several factors:

(1) Photoelectrons escaping from the surface induce a photoelectron current. This current I causes a voltage drop U across the sample with its resistance R, where $U_R = IR$. If the resistance R changes during the phase transition, a change of the surface potential is observed, which is given by

$$\Delta U_R = I\,\Delta R \approx I\frac{dR}{dT}\Delta T.$$

(2) The surface potential U, which is measured by XPS and can be as large as 10 V, arises from an electric field in the ferroelectric material and charges the sample as a capacitor C:

$$U = (Q_1 + Q_2)/C.$$

Here, Q_1 refers to the charging by the photoelectron current, and Q_2 is the surface charge due to the ferroelectric polarization. The capacitance C changes significantly near the Curie temperature causing a change of the surface potential ΔU_C, given by

$$\begin{aligned}\Delta U_C &\approx \frac{d\left(\frac{Q_1+Q_2}{C}\right)}{dT}\Delta T \\ &= \frac{1}{C}\frac{dQ_2}{dT}\Delta T - \frac{(Q_1+Q_2)}{C^2}\frac{dC}{dT}\Delta T - \frac{(Q_1+Q_2)}{C^2}\frac{dC}{dT} \\ &= -\frac{Uc}{C}\frac{dC}{dT}, \quad C = \varepsilon\varepsilon_0\frac{s}{d} \end{aligned} \tag{1}$$

and

$$\frac{dC}{dT} = \varepsilon\frac{s}{d}\frac{d\varepsilon}{dT}.$$

Therefore

$$-\frac{Uc}{C}\frac{dC}{dT} = -\frac{Uc}{\varepsilon}\frac{d\varepsilon}{dT}.$$

The first term in Eq. (1) takes into account the change in the surface charge due to the ferroelectric polarization, which changes significantly near the Curie temperature. The second term takes into account the change in the capacitance. The total deviation of the surface potential has three parts in total:

$$\Delta U = \Delta T\left(I\frac{dR}{dT} + \frac{1}{C}\frac{dQ_2}{dT} - \frac{U}{\varepsilon}\frac{d\varepsilon}{dT}\right). \tag{2}$$

Only the second term changes its sign if the polarization direction is reversed. For example, the sample prepolarized with the negative electrode on the surface where XPS measurements were carried out has a positive induced surface charge Q_2 below T_C. Above T_C this charge disappears (Fig. 7),
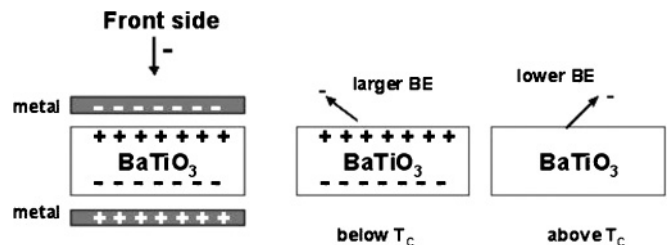

FIG. 7. Polarization and measurements.

such that $\frac{dQ_2}{dT} < 0$ and $\Delta U < 0$, as observed in the experiment (Fig. 4). Equation (2) does not take into account time-dependent effects such as the relaxation of any compensating charge.

V. SUMMARY

A sudden change (jump) in the surface potential was observed by XPS on a BaTiO$_3$ crystal surface at the Curie temperature. This change can be observed as a shift in the binding energy in the Ba $3d_{5/2}$ and Ti $2p$ core-level spectra recorded during heating and cooling of the crystal.

On the basis of theoretical and experimental data, we can conclude the following:

(1) The observed shift in binding energy is not a chemical shift but rather is related to surface charging.

(2) During cooling, there is a jump in the potential towards lower binding energy.

(3) The jump happens at T_C at least during cooling.

(4) The general trend is towards decreasing binding energy with increasing temperature.

(5) If the sample is prepolarized, the movement of domains is observed during heating at temperatures below T_C, and is accompanied by random shifts in the surface potential.

(6) There is an influence of the prepolarization direction on the jump.

(7) The direction of the energy jump in prepolarized samples coincides with the expected direction assuming ferroelectric polarization.

The study of the change in the surface potential induced by an applied electrical field could be a new way to detect a change in sample polarization. However, there are a few open questions about time-dependent effects and the behavior of the surface potential during temperature changes (e.g., a smooth shift in the binding energy at the beginning of the measurement). For example, the relaxation time for compensating charges on the sample surface during heating (cooling) of the crystal probably influences the shift in binding energy observed in the XPS spectra. The change in the surface potential of BaTiO$_3$ observed using XPS must be studied in more detail. A strong dependence of the surface potential on temperature, namely a phase transition, should be taken into account in the design of heterostructures consisting of ferroelectric materials, such as BaTiO$_3$.

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