I. INTRODUCTION

Bi$_4$Ti$_3$O$_{12}$ belongs to the family of mixed bismuth oxides with the chemical formula (Bi$_2$O$_2$)$_{2+}$$(\text{Me}_{x-1}R_xO_{3x+1})^{2-}$ first synthesized and described by Aurivillius. In the above formula, Me stands for a mono-, di-, or trivalent ion or a mixture of those; $R$ represents Ti$^{4+}$, Nb$^{5+}$, or Ta$^{5+}$; and $x=2, 3, 4$, etc. The crystal structure of Bi$_4$Ti$_3$O$_{12}$ can be described as a stacking of Bi$_2$O$_2$ layers and Bi$_2$Ti$_3$O$_{12}$ layers along the pseudotetragonal c axis (See Fig. 1 of Ref. 2). In the Bi$_2$Ti$_3$O$_{12}$ units, Ti ions are coordinated by oxygen octahedra, which form linear chains, and Bi ions occupy the interstitials outside the TiO$_6$ octahedra. It was pointed out in Ref. 2 that the Bi$_2$Ti$_3$O$_{12}$ unit has some similarity with the perovskite structure, and the height of the perovskite-type layer sandwiched between Bi$_2$O$_2$ layers is equal to six Ti–O distances or to three ABO$_3$ perovskite units.

According to some empirical rules, such a type of structure with highly charged cations surrounded by oxygen octahedra, which are linked through corners, is favorable for the occurrence of ferroelectricity, which was indeed found in Bi$_4$Ti$_3$O$_{12}$ by Subbarao. Recently, it was shown that ferroelectric Bi$_4$Ti$_3$O$_{12}$ thin films can find an application in electrooptic devices.

Another intriguing aspect of this material is its relation to high-$T_c$ oxide superconductors. As has been recently found, one of the phases of the Bi-Ca-Sr-Cu-O oxide superconductors family with $T_c \sim 80$ K has a structure analogous to that of Bi$_4$Ti$_3$O$_{12}$. In connection with this, some attempts for the search of different superconductors related with ferroelectric Bi$_4$Ti$_3$O$_{12}$ have been undertaken.

The electronic structure and chemical bonding of Bi$_4$Ti$_3$O$_{12}$ has not been studied up to now. In the present paper we present, to our knowledge, the first band-structure calculations along with the first measurements of x-ray photoelectron spectra (XPS) of the valence band and x-ray emission spectra (XES) of this compound, which give a direct information about the total and partial density of states distribution in the valence band.

II. EXPERIMENT

Single crystals of Bi$_4$Ti$_3$O$_{12}$ were grown using a modified Nacken–Kyropoulus crystal growth apparatus. The temperature was measured by a thermocouple of four thermocouples PtRh6% versus PtRh30% (EL 18) and a digital multimeter (sensitivity 0.1 μV). The multimeter and power supply of the resistance heating system were controlled by a computer.

According to the crystal growth experiments of Burton, the solution consisted of 68 mol% Bi$_2$O$_3$ (Johnson Matthey, Grade 1), 20 mol% Bi$_2$O$_3$ (Johnson Matthey, Grade 1) and 12 mol% TiO$_2$ (Merck, Optipur). The platinum crucible with the solution was placed on a ceramic support in the upper part of the heating system. The crystals were grown on small, thin (001) seeds. At a temperature of about 1270 K, they were carefully placed on the solution surface, where they stayed due to the surface tension. Temperature gradients up to 50 K/cm provide strong convection directed from the crucible wall to the center. As a result, the growing crystal was fixed in the middle of the crucible.

The cooling rate was 0.1 K/h at the beginning and 0.5 K/h at the end of the growth experiment. At a temperature of about 1200 K, the crystal was lifted from the solution using a platinum net and cooled down to room temperature at 15 K/h. Crystals of about 12 g and a thickness of up to 3 mm were obtained. Rectangular Bi$_4$Ti$_3$O$_{12}$ samples were cut and subsequently polished to optical quality.

Ti $L_α$ (2p$_{1/2}$–3d $4s$ transition) and OK $α$ (1s–2p transition) XES were measured with a x-ray spectrometer (RSM-500) with a diffraction grating ($N=600$ lines/mm; $R=6$ m) and electron excitation. In the course of XES measurements, all precautions were taken in order to avoid the decomposition of the sample, or its modification under the electron bombardment: a very soft regime with
a low current on the x-ray tube ($I=0.3\ mA$) was taken, and the position of the sample with respect to the electron beam was changed for each scan. The spectra were recorded in the first order of reflection by a secondary electron multiplier with CsI photocathode in an oil-free vacuum of $(1-2) \times 10^{-6}$ Torr. The entrance and exit slits of the spectrometer were $20\ \mu m$ wide, which gave an instrumental resolution Ti $L$ and O $K\alpha$ XES of about 0.9 and 1.2 eV, respectively. The x-ray tube was operated at $V=4.6\ keV$.

Ti $K\beta_5$ XES ($1s - 4p$ transition) was measured using fluorescent excitation with a Johan-type x-ray tube spectrometer with a position sensitive detector. [13] A (1011) plane of quartz curved to $R=2000\ mm$ was used as a crystal analyzer. The primary Cu $K$ radiation was used for the excitation of the Ti $K\beta_5$ spectra. The energy resolution was 0.3 eV. The sealed x-ray tube with a Cu anode was operated at $V=35\ keV$, $I=50\ mA$. The time of accumulation of the Ti $K\beta_5$ spectra was about 50 h.

**X-ray photoelectron and core-level spectra of Bi$_4$Ti$_3$O$_{12}$**

were measured using an ESCA spectrometer of Perkin-Elmer (PHI 5600 ci, monochromatized Al $K\alpha$ radiation, FWHM=0.3 eV). The resolution of the concentric hemispherical analyzer was adjusted to less than $\Delta E=0.2\ eV$. A single crystal of Bi$_4$Ti$_3$O$_{12}$ was cleaved in high vacuum prior to the XPS measurements. The spectra were calibrated using the C 1s line of small carbon contaminations of the surface as a reference level ($E=285.0\ eV$). A survey XPS from the valence-band region is shown in the upper panel of Fig. 1.

The unmarked feature at a binding energy of 23.5 eV is due to partial decomposition of the sample in the course of measurements that resulted in the formation of metallic Bi at the sample surface. In order to avoid the charging, it was necessary to irradiate the sample with low kinetic energy electrons ($E_{kin}\leq 100\ eV$). In the lower panel of Fig. 1, the evolution of the spectrum with the measurement time is shown. It has not been investigated whether the decomposition of the sample was caused by electrons or x-ray photons.

Based on the measured binding energies of the core levels from XPS (531.50 eV for O 1s, 459.80 eV for Ti 2p$_{3/2}$), it is possible to align the x-ray photoemission spectrum of the valence band and the individual x-ray emission spectra to a common energy scale with respect to the Fermi level. Since for dielectric materials the error of several eV in relative positions of the spectra due to charging effects is difficult to overcome, we had to displace the spectra slightly in order to match the positions of the valence band in the XPS and in the XES of components. More detailed structure of the valence band XPS and XES on a common energy scale is shown in Fig. 2.

**III. STRUCTURE MODEL AND ELECTRONIC STRUCTURE CALCULATIONS**

The crystal structure of Bi$_4$Ti$_3$O$_{12}$ has been determined from x-ray and neutron diffraction experiments by Dorrian et al. [8] and was afterwards refined by David Rae et al. [9] The material was found to be a displacive ferroelectric with polar orthorombic structure, with four formula units per unit cell and the lattice parameters $a=5.45\ \AA$, $b=5.41\ \AA$, $c=32.83\ \AA$. The space group is $B2cb$ according to Ref. [8] and $B1a1$ as found in Ref. [9]. Any of these orthorombic structures is a commensurate modulation of the nonpolar orthorombic parent $Fmmm$ structure, which is derived from the idealized tetragonal $I4/mmm$ structure. Bi$_4$Ti$_3$O$_{12}$ exists in a $Fmmm$ structure above the ferroelectric transition temperature of 675 $^0C$.

We performed *ab initio* band-structure calculation within the local density approximation (LDA), with the exchange-correlation potential parametrization according to von Barth and Hedin [11] and gradient corrections as proposed by Langreth and Mehl. [12] In spite of some argument that the multielectron correlation effects beyond the LDA play a role in the formation of electronic structure of titanium oxides [16], the only noticeable effect of correlations, if any, seems to be confined to the core-level region [17]. Therefore, one may expect the LDA to provide an adequate description of the occupied electronic states within the valence band.

Specifically, we used the tight-binding linear muffin-tin orbital method (TB-LMTO) in the atomic sphere approximation (ASA) [15], which was proven to be quite accurate and efficient in many applications. Even with this method, the electronic structure calculation of the real orthorombic phase with 76 atoms per unit cell poses a problem. It is even more complicated by the fact that the crystal structure is rather open, apart from the chains of Ti-O octahedra, which are intersected by warped Bi-O-Bi layers. In order to provide an adequate description of the potential over the unit cell, the structure has to be packed with additional empty spheres, which increase the basis set and the complexity of the computational problem even further.

In order to keep the computational effort in our band structure calculations manageable and to simplify the analysis of underlying trends in the electronic structure of the material, we preferred to perform calculations for the idealized $I4/mmm$ crystal structure. It is a body-centered tetragonal structure for which we used lattice parameters $a=7.2558\ a.u.$ (=√3ab/2 of the orthorombic structure) and $c/a=8.55$. We used the atomic positions listed in Table 6 (Model 3) of Ref. [8] and averaged them over sites that become equivalent in the $I4/mmm$ structure. The resulting positions of atoms and empty spheres (E1 to E4) are listed in Table 1.

The positions of the atoms may easily be seen from the charge density plots in two different planes cutting
the unit cell, as obtained from self-consistent TB-LMTO calculation (Fig. 3). Due to the inversion symmetry, only half of the unit cell is shown. Moreover, a $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ translation maps the atoms and the charge density pattern onto itself. In the actual orthorhombic structure, O4-Ti2-O3-Ti1-O3-Ti2-O4 chains of joined TiO$_6$ octahedra are rotated around the c axis by up to 7.5° (in the opposite direction for adjacent chains), shifted in the plane normal to c, and a tilting up to 6.5° appears for octahedra within each chain. These distortions, which are well described in Ref. [5], are not negligible but they are expected to have only a moderate effect on the basic band-structure properties, because the atomic coordination and distances between near neighbors are essentially preserved. Since in the present work we are mostly concerned with spectroscopic information that is accumulated from crystallographically inequivalent atoms anyway and do not discuss the aspects of ferroelectric behavior, our structure model used in the calculations seems to be justified.

The choice of the radii of space-filling atomic spheres for a LMTO-ASA calculation is not unique for compounds, especially for those including several types of atoms with different electronegativity. Our choice was based on a compromise between possibly good matching of potentials at the sphere boundaries for all types of atoms and possibly low spheres overlap which we managed to keep below 30% of all interatomic distances. The final values of the atomic sphere radii together with the boundary values of the potential, adjusted in the course of iterations, are listed in Table II along with the self-consistent partial charges inside the spheres. There is not much sense to consider the net charge $\Delta Q$ within each atomic sphere, which is listed in the last column of Table II, as direct reference to a charge state of the atoms in the compound, because this property of course depends on the definition and may vary considerably as based on the different estimates. It is reasonable, however, to analyze the changes of $\Delta Q$ from one crystallographically inequivalent position to another within the same chemical species, because this gives clear indication of the charge transfer. The partial densities of states (DOS) of the components as obtained from TB-LMTO calculations using the tetrahedron method with 140 k points in the irreducible part of the Brillouin zone are shown in Figs. 1, 2, and 3.

IV. RESULTS AND DISCUSSION

As is seen from Fig. 3, the Ti atoms in Bi$_4$Ti$_3$O$_{12}$ are surrounded by almost perfect O$_6$ octahedra. With Bi1 and Bi2 atoms occupying the pores formed by 12 oxygen atoms of adjacent octahedra, a perovskite-type sequence of layers is formed: (Bi2-O4); (O5-Ti2-O5); (Bi1-O3); (O1-Ti1-O1); (Bi1-O3); (O5-Ti2-O5); (Bi2-O4). The corresponding repeated perovskite structure with the chemical formula BiTiO$_3$ may, however, not be stable due to electrostatic considerations. The system gets stabilized by interchanging three perovskite-type layers with an additional O2 plane. This is accompanied by considerable warping of (Bi2-O4) planes and a noticeable [001] displacement of the Ti2 atoms from the middle of O6 octahedra surrounding them.

According to our calculations, the 3d DOS at the Ti1 site (Fig. 3) is rather similar to that known for perovskite materials as BaTiO$_3$ and PbTiO$_3$ (see, e.g., Ref. [19,20]) – the Ti3d states are concentrated at the bottom of the broad (about 5 eV) valence band. Correspondingly, the O 2p DOS at the O1, O3 and O5 sites (Fig. 3) are rather typical for oxygen in perovskites, with a pronounced maximum near the top of the valence band where O2p states are nonbonding. The nonsphericity of the charge density around the displaced Ti2 atom in its oxygen cage is quite similar to that around Ti in tetragonally distorted BaTiO$_3$ (see Fig. 4 of Ref. [5]).

A considerable difference in the $\Delta Q$ values at the Ti1 and Ti2 sites is only partially due to a small differences in the atomic sphere sizes, but comes mostly from a strong dynamic charge transfer along the Ti2-O4 bond that occurs as this bond length is varied. This effect is well known for Ti-based perovskite systems and is the driving force for tetragonal ferroelectric instability in BaTiO$_3$ and PbTiO$_3$. Quantitatively, this charge transfer or dynamic polarization of the Ti-O bond is characterized by Born effective charges, which were calculated by Zhong et al. [21] to be $+7$ at the Ti site and $-5$ at the O site (as displaced towards Ti) in BaTiO$_3$ and PbTiO$_3$, i.e., very different from nominal ionic valence values.

The reason why the O4 atoms acquire positive net charge in our calculations rather than become more electronegative as Ti2 comes closer, is that the charge distribution at the O4 sites is far from being spherical symmetric and well localized. O4 terminates the chain of TiO$_6$ octahedra and is separated from the Bi2 atom by an interstitial where we put an empty sphere E4. The charge transferred from Ti2 towards O4 is, therefore, partially attributed to E4 (and also to E1) empty spheres in our calculation. The energetics of the 2s states (Fig. 3) reveals that the effective potential is indeed less attractive for electrons at the O4 as compared to all other oxygen positions, thus indicating higher electronegativity, due to the Ti2$\rightarrow$O4 charge transfer. Correspondingly, the center of gravity of the O 2p states is shifted to higher energies at the O4 site. Since the valence band is essentially formed by hybridized O 2p, Ti 3d and Bi 6p states, the presence of only one Ti neighbor and the remoteness of the Bi neighbors to the O4 site isolates the O 2s states to a narrow flat band and reduces the effective width of the O4-2p partial DOS.

The O2 sites, in difference to the other oxygen sites, which belong to the octahedra cage, form a basal plane for empty pyramids, or semiocctahedra, with the apical points (the by O4 atoms) protruding up or down from the O2 plane in a chessboard configuration. The O2 atoms mediate the interaction between two Bi2 layers, and the
2p states of O2 exhibit noticeable hybridization with the 6s and 6p states of Bi2.

Summing up over all oxygen sites, the O 2p partial DOS is asymmetric, with states near the top of the valence band dominating in the perovskite layers, and narrow band related to O4 sites giving the main contribution again at the upper half of the valence band. This state distribution is well revealed in the O Kα x-ray emission spectrum (Fig. 1 lower panel), which probes the 1s−2p transition and thus is expected to scan the occupied part of the O 2p partial DOS.

The x-ray spectra of Ti are shown in Fig. 1. The Ti Kβ spectrum probes the occupied part of the Ti 4p DOS. The lower of two pronounced peaks separated by ~15 eV reveals the admixture of Ti 4p states to the O 2s band. This energy separation is typical for all oxides and is well reproduced in the band structure calculation.

The Ti L spectrum consists of two subbands (Lα and Lβ, see Fig. 2) which correspond to x-ray transitions with a valence band electron filling the core vacancy in the 2p3/2 or 2p1/2 level, correspondingly. Since the Ti 3d DOS in the valence band dominate those of the Ti 4s as is seen in Fig. 1 (note the different scales for 3d and 4s DOS), both subbands essentially reveal the same Ti 3d DOS distribution, modulated by a slightly different energy dependence of the dipole transition matrix elements for 2p1/2 and 2p3/2 processes, and somehow overlap. In order to enable the comparison with the calculated DOS, we cut the experimental TiLα, β spectrum near the minimum and shifted the upper part downwards by 5.5 eV, that is the value of the Ti 2p3/2−2p1/2 splitting in TiO2. Thus overlapped spectra, when compared with the calculated Ti 3d DOS (Fig. 1 right panel), reveal all essential features of the occupied part of the Ti 3d band.

According to our band-structure calculation, the two inequivalent types of Bi sites have quite different partial DOS, which reveals the differences in their crystallographic environment. The 6s states of Bi1 atoms, which belong to the perovskite-like “BiTiO4” fragment of the crystal lattice, are filled and separated from the valence band by a gap of about 3 eV. The split-off Bi 6s band of about 1 eV width is slightly hybridized with O 2p states at the neighboring O1, O3 and O5 sites (see Fig. 3). Some small fraction of the Bi 6s states is moreover admixed to the low-lying O 2s states and to the higher states in the valence band. The partial DOS of Bi1 closely resembles that of Pb in PbTiO3 (a tetragonally distorted perovskite, see Fig. 3 of Ref. [24]), with the only difference that the 6s states of Bi, which have one electron more than Pb, are deeper (by ~2 eV with respect to the valence band), more localized and exhibit less admixture to the states in the valence band.

The 6p states of Bi1 participate mostly in the valence band, forming a pronounced bonding peak due to the hybridization with O 2p states at ~−5.2 eV. This bonding state is visible in the O 2p DOS at O1, O3 and to a smaller extent at O5 sites. There is no essential charge transfer from the Bi1 to the neighboring O atoms. On the contrary, the large atomic sphere at the Bi1 site accumulates some extra charge (due to charge transfer from Ti) as compared to the free Bi atom.

In contrast to this, Bi atoms, which belong to Bi2–O2 warped planes, exhibit a considerable loss of charge due to a more polar type of the underlying bonding than that in the perovskite-like fragments. The Bi2-6s states are not fully occupied and participate in the chemical bonding. The partial DOS at the Bi2 site, with a ~3 eV broad Bi 6s band, is not resolved in the measured spectroscopic data. The position of the next distinct peak (at ~−10 eV in Fig. 7), which reveals the Bi 6s states, is again correctly predicted in the LMTO calculation. It seems possible that the calculation overestimates the splitting of the Bi 6s peak (into two energetically separated parts related to the Bi1 and Bi2 sites) that would otherwise be detected in XPS at a given energy resolution. This discrepancy may be probably eliminated in a calculation considering a more exact structure model, where the relaxation of the TiO6 fragments makes the potentials at inequivalent Bi sites more similar.

The XPS peak at about ~19 eV in Fig. 1 which reveals the contribution from the O 2s states, lies approximately 2.5 eV below the position of the O 2s states according to the LMTO calculation. This discrepancy is typical for LDA-based electronic structure calculations of oxides, as compared to XPS results, and is seemingly due to the effect of the hole relaxation, which effectively increases the binding energy of an electron leaving a comparatively localized state such as Oi 2s. This effect remains beyond the LDA, but may be correctly accounted for by more accurate treatment of correlation effects, e.g., in a GW approximation, as was shown for MgO in Ref. [25]. This effect is smaller for less localized states in the valence band.

Another discrepancy between the calculation and XPS is that the split-off narrow peak associated with O 2s states of O4 atoms is not resolved in the measured spectrum. It is not clear at the moment whether the realistic geometry with relaxed TiO6 octahedra smears out the difference between O4 and other oxygen sites. The effect of the O 2s holes, which should be stronger for more localized O4-2s states, also tends to increase the binding energy for the latter and thus to lower their separation from other O 2s states in the XPS. It may also well be the case that two marked discrepancies from the experimental spectra (the splittings of the Bi 6s and O 2s bands) are due to the crudeness of ASA when applied to a quite open structure of Bi2Ti3O12, that can be checked in subsequent calculations not using any shape approximation.
V. CONCLUSION

In the present paper, we present an analysis of the electronic structure of Bi$_4$Ti$_3$O$_{12}$ by different spectroscopic techniques (XPS and x-ray emission spectroscopy), combined with an ab initio band-structure calculation. It was studied how the observed valence-band spectra are formed by contributions from crystallographically inequivalent types of Ti (two species), Bi (two species) and O (five species) atoms in the idealized 14/mmm structure. The main difference in the charge state and the type of chemical bonding is between those species of Bi and O, which belong to perovskitelike fragments, on the one hand, and to intermediate Bi–O planes on the other hand. The electronic structure related to perovskitelike fragments has many common features with those of perovskite-type compounds BaTiO$_3$ and PbTiO$_3$, whereas the intermediate Bi–O planes reveal some similarity with the bismuth oxides.

ACKNOWLEDGMENTS

Financial support by the Deutsche Forschungsgemeinschaft (SFB 225), the NATO (grant No. HTECH.LG940861), and the Russian Foundation for Fundamental Research (grant No. 94-03-08040) is gratefully acknowledged. One of us (E.Z.K) wants to thank for the kind hospitality at the University of Osnabrück during his stay.

REFERENCES

[1] B. Aurivillius, Ark. Kemi 1, 463 (1949); 1, 499 (1949); 2, 519 (1950).
[2] E. C. Subbarao, Phys. Rev. 122, 804 (1961).
[3] J. F. Dorrian, R. E. Newnham, D. K. Smith, and M. I. Kay, Ferroelectrics 3, 17 (1971).
[4] M. Takashige, H. Suzuki, and S. Sawada, Ferroelectrics 96, 281 (1989).
[5] A. David Rae, J. G. Thompson, R. L. Withers, and A. C. Willis, Acta Crystallogr. Sec. B 46, 474 (1990).
[6] B. Frit and J. P. Mercurio, J. All. Comp. 188, 27 (1992).
[7] B. T. Matthias, Science 113, 591 (1951).
[8] A. David Rae, J. G. Thompson, R. L. Withers, and A. C. Willis, Acta Crystallogr. Sec. B 46, 474 (1990).
[9] W. Jo, H.-J. Cho, T. W. Noh, B. I. Kim, Z. G. Khim, D.-S. Kim, and S.-I. Kwun, Appl. Phys. Lett. 63, 2198 (1993); W. Jo and T. W. Noh, ibid. 65, 2780 (1994).
[10] H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. 27, L201 (1988).
[11] T. M. Burton, J. Cryst. Growth 136, 2595 (1993); K. Okada and A. Kotani, J. Electron Spectrosc. Relat. Phenom. 62, 131 (1993).
[12] The Ti 2p satellites observed in the XPS of TiO$_2$ seem to be mostly due to inelastic loss processes, but the correlation effects may well play a certain role in the satellite formation. These aspects are now specially investigated for TiO$_2$ and will be reported elsewhere; in Bi$_4$Ti$_3$O$_{12}$, no clear Ti 2p satellite structure was observed, because of the overlap with Bi 4d states.
[13] N. I. Medvedeva, V. P. Zhukov, and V. A. Gubanov, Fiz. Tverd. Tela (Leningrad) 32, 1865 (1990). [Sov. Phys. Solid State 32, 1087 (1990)].
[14] U. Schönberger and F. Aryasetiawan, Phys. Rev. B 52, 2533 (1995). (unpublished).

FIG. 1. Upper panel: x-ray photoelectron spectrum of Bi$_4$Ti$_3$O$_{12}$. Lower panel: Bi 5d-related part of the spectrum (from different sample) immediately after the fracture (dots) and after 24 h of irradiation (solid line).

FIG. 2. x-ray photoelectron spectrum and x-ray emission O Kα, Ti Lα, Ti Lβ and Ti Kβ spectra of Bi$_4$Ti$_3$O$_{12}$.

FIG. 3. Charge density contour plots in the (010) and (110) planes of Bi$_4$Ti$_3$O$_{12}$ as calculated by TB-LMTO method.
FIG. 4. Calculated partial DOS at Ti1 and Ti2 sites and Ti x-ray emission spectra of Bi$_4$Ti$_3$O$_{12}$. Left panel: 4\(p\) (above); total Ti 4\(p\) DOS per unit cell (below); Ti K\(\beta\) spectrum (dots, below). Right panel: 4\(s\) (above, dashed line, left scale); 3\(d\) (above, solid line, right scale); total Ti 3\(d\) DOS per unit cell (below); Ti L\(\alpha\), L\(\beta\) spectra (dots, below).

FIG. 5. Calculated local DOS at five inequivalent oxygen sites in Bi$_4$Ti$_3$O$_{12}$ (upper panels); total O 2\(p\) DOS per unit cell (lower panel, solid line) and O K\(\alpha\) emission spectrum (dots).

FIG. 6. Calculated 6\(s\) and 6\(p\) partial DOS at Bi1 and Bi2 sites of Bi$_4$Ti$_3$O$_{12}$.

FIG. 7. x-ray photoelectron spectrum of the valence band (dots) and calculated total DOS of Bi$_4$Ti$_3$O$_{12}$ (solid line). Note the change of scale for XPS at −13 eV.

TABLE I. Atomic coordinates in the \(I4/mmm\) structure.

| Site | Wyckoff notation | \(x\) | \(y\) | \(z\) |
|------|------------------|-------|-------|-------|
| Bi1  | 2\(e\)          | 0     | 0     | 0.0668|
| Bi2  | 2\(e\)          | 0     | 0     | 0.2113|
| Ti1  | 1\(b\)          | 0     | 0     | \(\frac{1}{2}\) |
| Ti2  | 2\(e\)          | 0     | 0     | 0.3713|
| O1   | 2\(c\)          | \(\frac{1}{4}\) | 0     | 0     |
| O2   | 2\(d\)          | \(\frac{1}{4}\) | 0     | \(\frac{1}{4}\) |
| O3   | 2\(e\)          | 0     | 0     | 0.4410|
| O4   | 2\(e\)          | 0     | 0     | 0.3185|
| O5   | 4\(g\)          | \(\frac{1}{2}\) | 0     | 0.1175|
| E1   | 8\(m\)          | 0.2435| 0.2435| 0.1601|
| E2   | 4\(g\)          | \(\frac{1}{2}\) | 0.2435| 0.1824|
| E3   | 2\(e\)          | 0     | 0     | 0.1383|
| E4   | 2\(e\)          | 0     | 0     | 0.2740|

TABLE II. Atomic sphere radii \(S\) used in the calculation; potential values at the sphere boundaries \(V(S)\); partial s, \(p\), and \(d + f\) electron occupation numbers and net electrostatic charges \(\Delta Q\) within atomic spheres.

| Site | \(S\) (a.u.) | \(V(S)\), Ry | \(Q_s\) | \(Q_p\) | \(Q_{d+f}\) | \(\Delta Q\) |
|------|--------------|---------------|--------|--------|-------------|------------|
| Bi1  | 3.6          | −0.739        | 2.067  | 1.921  | 1.281       | −0.269     |
| Bi2  | 3.2          | −0.708        | 1.800  | 1.193  | 0.757       | +1.250     |
| Ti1  | 2.5          | −0.903        | 0.375  | 0.726  | 1.945       | +0.954     |
| Ti2  | 2.3          | −0.885        | 0.224  | 0.397  | 1.549       | +1.830     |
| O1   | 2.0          | −0.810        | 1.740  | 4.465  | 0.030       | −0.235     |
| O2   | 2.1          | −0.727        | 1.724  | 4.777  | 0.031       | −0.232     |
| O3   | 2.0          | −0.799        | 1.741  | 4.420  | 0.027       | −0.188     |
| O4   | 2.0          | −0.758        | 1.653  | 4.180  | 0.016       | +0.151     |
| O5   | 2.1          | −0.737        | 1.770  | 4.443  | 0.030       | −0.243     |
| E1   | 1.8          | −0.707        | 0.179  | 0.143  | 0.058       | −0.380     |
| E2   | 1.7          | −0.580        | 0.093  | 0.064  | 0.018       | −0.175     |
| E3   | 1.7          | −0.515        | 0.063  | 0.047  | 0.014       | −0.124     |
| E4   | 1.6          | −0.722        | 0.169  | 0.107  | 0.034       | −0.310     |
