Oxygen 1s x-ray absorption of $BaPb_{1-x}Bi_xO_3$

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Oxygen 1s x-ray-absorption spectra of the $BaPb_{1-x}Bi_xO_3$ system have been measured. The spectra do not show the prepeak structures common in the doped copper oxide superconductors. The observed shift of the first peak is much smaller than predicted by single-particle density-of-states calculations.

I. INTRODUCTION

The $BaPb_{1-x}Bi_xO_3$ compounds are perovskites. Their electronic properties vary considerably as a function of x and because for $x=0.25$ a superconducting state was found up to 13 K,[1] this system was much studied in the last decade.[2] Although originally overshadowed by the development of the high-T_c copper-oxide-based superconductors, the $BaPb_{1-x}Bi_xO_3$ compounds are still of interest and their study received additional impetus from the discovery of T_c up to 30 K in the related $Ba_{1-x}K_xBiO_3$ materials.[3] It is known that the group of (Ba,K)(Pb,Bi)O₃ perovskite compounds have some properties, like an exceptionally high ratio of T_c to the linear specific-heat coefficient, in common with the copper-oxide-based superconductors.[4] This of course opens the question of possible similarities in the mechanism causing superconductivity.

One of the important diagnostic techniques for the determination of the electronic structure of the copper-oxide-based superconductors was x-ray absorption (XAS), and more specifically oxygen 1s XAS (Refs. 5 and 6) and the related electron-energy-loss technique (EELS).[7] Because of the site and symmetry selectivity of oxygen 1s XAS it was possible to show the nature of the states responsible for superconductivity. The results showed the growth of a prepeak as a function of the doping concentration; this indicates the introduction of hole states, with predominantly oxygen $2p$ character, in the gap as the insulating parent compounds, like La_2CuO_4 and $YBa_2Cu_3O_6$, are doped with holes. One of the objectives here will be to see whether similar prepeaks exist in the $BaPb_{1-x}Bi_xO_3$ compounds.

The question of "gap states" relates also to the origin of the band gap in the parent compounds. For the copper-oxide-based superconductors it is now clear that the band gap is caused by Mott-Hubbard correlation, but spectroscopic studies and cluster calculations showed that the lowest-energy excitations across the gap actually have predominantly charge-transfer character.[8] Following the Zaanen-Sawatzky-Allen model this means that the Mott-Hubbard correlation in the Cu $3d$ band (U) is

much larger than the charge transfer to the oxygen (Δ), indicating that if holes are created they will have mainly oxygen $2p$ character.[9] Oxygen 1s XAS does not give direct evidence on such gaps, but it can be used to see if the spectral function is similar to the predictions from single-particle density-of-states calculations or if correlation effects have to be taken into account explicitly (as for the copper-oxide-based superconductors).

A final question which we believe may be partly answered by oxygen 1s XAS relates to the possible models that may describe the influence of substitution of lead by bismuth. Here one can imagine models as a combined rigid band shift or the formation of superstructures due to (partial) ordering or lead and bismuth.

II. DENSITY OF STATES FROM ELECTRONIC-STRUCTURE CALCULATIONS

To understand the questions addressed here it is necessary to consider the results of single-particle density-of-states calculations from the literature.[2,10–14] For the purpose of this paper the density-of-states calculation of Takegahara and Kasuyo,[11] reproduced in Fig. 1, may be considered representative.[15] These calculations show that the occupied states around the Fermi energy are dominated by oxygen $2p$ character, while the unoccupied states have mostly lead-bismuth and barium character. The main structure of the lead and bismuth compounds is rather similar but the Fermi level appears at higher energy with respect to these structures in the bismuth compound because bismuth has one more electron. $BaPbO_3$ is calculated to be metallic in accord with experiment; the number of charge carriers is of the order of 1×10^{20} cm⁻³.[16] For the bismuth compound experiment finds a band gap of 0.3 eV (activation energy)[17] in contrast to the metallic result of the calculation. This discrepancy is attributed to a charge-density fluctuation, with a tendency towards disproportionation of the bismuth sites into Bi^V and Bi^{III}.[2] The existence of two different bismuth sites is confirmed by bismuth 1s extended x-ray-absorption fine structure (EXAFS),[18,19] but in bismuth $4f$ x-ray photoemission spectroscopy (XPS) (Refs. 20–22) no clear indi-

cation for charge disproportionation is found.

Considerable effort has been put into trying to find suitable schemes to interpolate between the $BaPbO_3$ and $BaBiO_3$ limits and in order to explain the changes in (super) conductivity as a function of composition. Spectral studies of the occupied levels have also been made by photoemission and they show negligible shift of the oxygen $2p$ levels as a function of composition[20,23−27] in contrast to the calculated density-of-states results (see Fig. 1). In this paper we will follow the trends of the unoccupied states in the oxygen $1s$ XAS spectra, which should closely reflect the partial density of oxygen $2p$ states (which in turn reflect the peaks in the total density of states) as shown in Fig. 1. Our results will in fact show that there is as little agreement between theory and experiment for the unoccupied states as for the occupied states and that in both cases the problem lies in a much smaller experimental shift than predicted between the observed structures in $BaPbO_3$ and $BaBiO_3$.
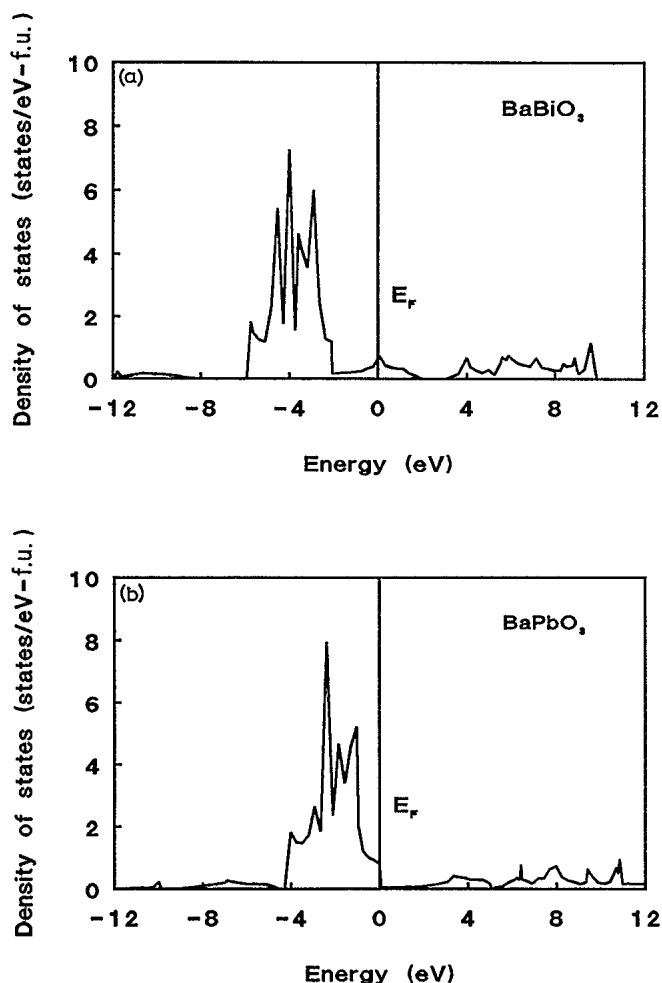

FIG. 1. The oxygen p-projected density of states for (a) $BaBiO_3$ and (b) $BaPbO_3$ as calcualted in Ref. 11.

III. EXPERIMENTAL

The x-ray absorption measurements were carried out at the Berliner Elektronenspeicherring Gesellschaft für Synchrotronstrahlung (BESSY), using the SX700(I) plane grating monochromator.[28] The experimental resolution was 0.5-eV full width half maximum (FWHM). The spectra were recorded in total-electron-yield mode and were normalized to the beam current. The pressure during measurements was in the 10^{-10}-Torr range. To calibrate the energy we measured TiO_2, and vanadium metal, using the EELS data of Fink et al.[29] as reference.

The samples were prepared in air by solid-state reaction of $BaCO_3$, PbO_2, and Bi_2O_3 powders with two intermittent regrindings. For the final heat treatment the powders were pressed into pellets. Each heat treatment lasted 24 h. For samples up to $x = 0.5$ a temperature of 880°C was used in the final sintering, for the higher bismuth concentrations a slightly lower temperature of 830 °C was used. X-ray diffraction confirmed the lattice structure and no evidence for impurity phases was observed. The pellets were mounted with conducting paste to a grounded sample holder and placed in the UHV system. At a pressure of about 10^{-9} Torr the samples were scraped with a ruby file. The reproducibility was tested by rescraping.

To compare the calculated oxygen p density of states to experiment, the density of states is broadened with a Lorentzian of 0.3 eV to simulate the core-hole lifetime and convoluted with a Gaussian of 0.5 eV to simulate the experimental resolution of the SX700(I) monochromator. As threshold we used the oxygen $1s$ XPS peak position, which was found to be at a constant value of 529.1 eV throughout the series.[30]

IV. RESULTS AND INTERPRETATION

The oxygen $1s$ x-ray-absorption spectra of ten $BaPb_{1-x}Bi_xO_3$ compounds are shown in Fig. 2. The overall shape of the spectra is similar and shows three distinct features in the first 15 eV above the edge. Unambiguous assignment of these peaks to features in the partial density of states of Fig. 1 is difficult, partly because the density-of-states calculation is unreliable at higher energies (because the basis set and energy window of linearization are insufficient) and partly because of the absence of XAS matrix elements and possibly the neglect of the core-hole effects.[31]

In Fig. 3 we compare x-ray absorption and oxygen-p-projected density of states for $BaPbO_3$ and $BaBiO_3$. We tentatively assign the peak at ∼536 eV, approximately 7 eV above threshold, to the major peak seen in the calculated density of states about 9 eV above E_F in $BaPbO_3$ and about 6 eV above E_F in $BaBiO_3$. This major feature changes shape somewhat as a function of composition but shifts considerably less than in the calculation.

The most interesting peak in the spectra of Fig. 2 is that nearest threshold which shifts gradually from 529.8 eV for $BaBiO_3$ to 531.1 eV for $BaPbO_3$. This shift is again much smaller than the shift predicted by the density-of-states calculation where a shift of ∼3 eV is

seen, together with some modifications of the shape. Neither can we see any prepeak structure growing as a function of composition as was the case in copper-oxide-based superconductors like $YBa_2Cu_3O_{7-\delta}$ and $La_{2-x}Sr_xCuO_4$. In this our results disagree with the previously published oxygen 1s XAS data,[32] where the authors claim the appearance of an extra feature at threshold as a result of "Bi-doping." The total absence of this prepeak structure was confirmed by measurements taken with higher monochromator resolution.[33,34] We stress that this marks a clear distinction with the copper-oxide-based superconductors, where the prepeaks due to doping-induced gap states are very important.

V. DISCUSSION

For us the central discrepancy is that found for $BaPbO_3$ between the density of states and the oxygen 1s XAS peak positions (see Fig. 3). The following points will be discussed: the influence on the spectral function
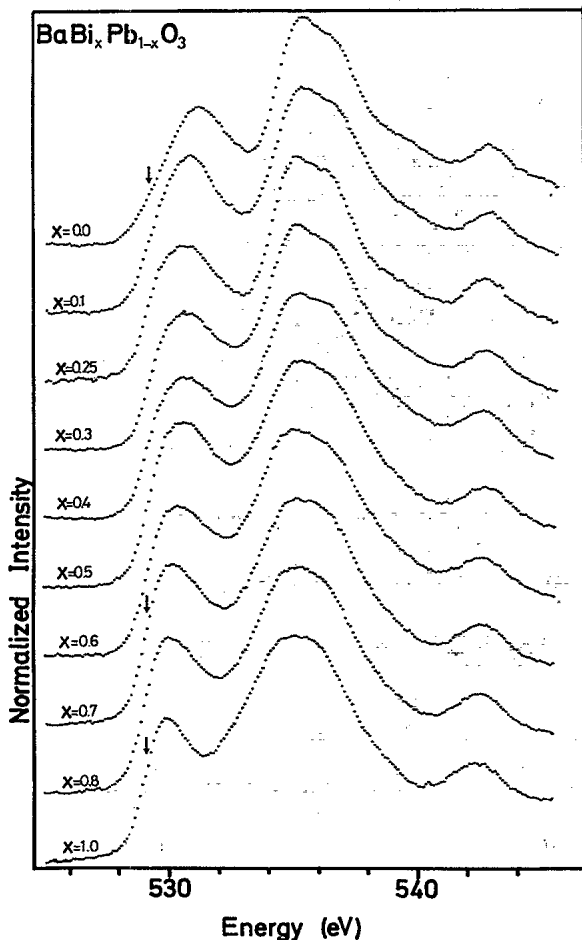
of the core hole, limitations of the single-particle approach, stoichiometry effects, and modifications in the density of states due to a calculation in the real crystal structure and to relativistic effects.

A. Core-hole effect

An effect which can play a role is the influence of the core hole. The spectral function of XAS relates, according to the final-state rule, to the final-state density of states. In general it can be stated that the core hole will
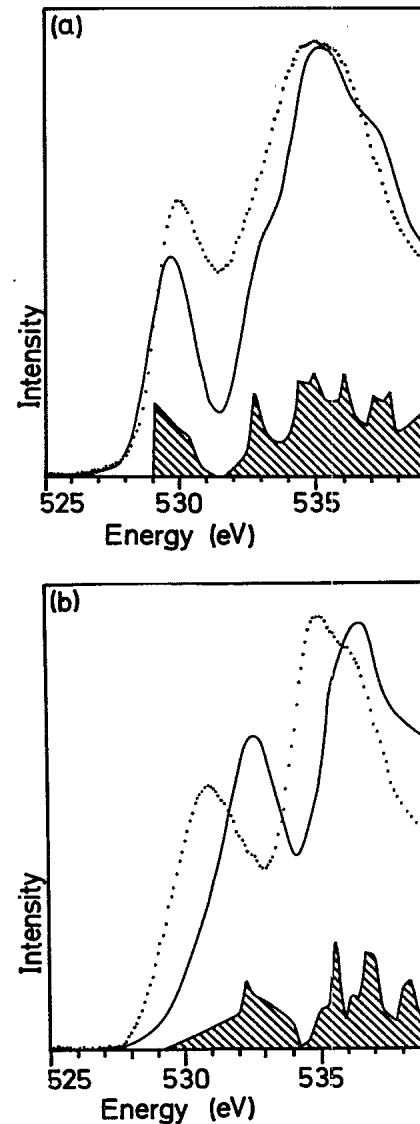

FIG. 2. Oxygen 1s x-ray-absorption spectra of a series of ten $BaPb_{1-x}Bi_xO_3$ compounds, measured with the SX700(I) monochromator at BESSY.

FIG. 3. Comparison of the SX700(I) results with the broadened oxygen p density of states from Ref. 11. Comparisons are made for (a) $BaBiO_3$ and (b) $BaPbO_3$. The oxygen p density of states is given by the hatched area. The solid line gives the density of states broadened with a Lorentzian of 0.3 eV (FWHM), to simulate intrinsic broadenings, and a Gaussian of 0.5 eV (FWHM) to simulate the experimental resolution.

cause a shift of spectral weight to lower energies due to the attractive core-hole potential.[35] However, we know of no case where oxygen 1s XAS peaks are shifted by as much as 2 eV, which would be necessary to explain the present results.[31]

B. Limitations in the single-particle approach

A second reason for the discrepancy are modifications induced by the single-particle approximation: Strictly speaking eigenenergies in a density of states should not be equated with ionization energies and electron affinities. Ground-state self-energy shifts can have a large effect on the gaps calculated for insulators but generally have a small effect for states near E_F in metals.[36,31]

C. Stoichiometry effects

According to Takegahara and Kasuyo,[11] the discrepancy of the energy positions for BaPbO$_3$ can be due to extra oxygen vacancies which will shift the Fermi level. Because of the low density of states just above E_F this effect can be considerable. For the related BaSn$_{1-x}$Sb$_x$O$_{3-\delta}$ system, samples which were prepared differently showed differences in resistivity measurements, but from accurate weight measurements it was found that δ was maximally 0.01.[37] To test this option for BaPbO$_3$ we repeated the XAS experiments for six samples prepared at different temperatures to influence the vacancy concentrations. They again had different resistivities and Hall coefficients,[38] but all oxygen 1s XAS spectra were found to be identical and no shift was observed. From this we conclude that nonstoichiometry effects are unlikely to explain the discrepancy found.

D. Crystal structure and relativistic effects

Another factor which can play a role is that the calculations are performed in an ideal cubic structure. Mattheiss and Hamann[2] have repeated the calculations for BaBiO$_3$ and BaPb$_{0.7}$Bi$_{0.3}$O$_3$ for the real orthorhombic and tetragonal crystal structures and the differences are found to be small. Comparison of the projected oxygen p density of states of BaPb$_{0.7}$Bi$_{0.3}$O$_3$ in both crystal structures, results in a shift of the peak position, after broadening, of only about 0.2 eV. From these results it can be expected that also for BaPbO$_3$ only minor effects are to be expected. A further approximation in the calculations is the treatment of the relativistic effects; in Refs. 2 and 11 a scalar description is used. Mattheiss and Hamann say that the spin-orbit coupling, neglected in their calculations, should only shift E_F for $\sim$0.1 eV, but we are measuring peaks that are more Pb in character and that are predicted some eV away from E_F. We cannot tell if the approximations are less valid for such peaks, but suggest that this is one line of questioning that should be followed up.

E. Concentration dependence

A final problem relates to the electronic structure model for mixed BaPb$_{1-x}$Bi$_x$O$_3$. In Fig. 4 we plot the posi-
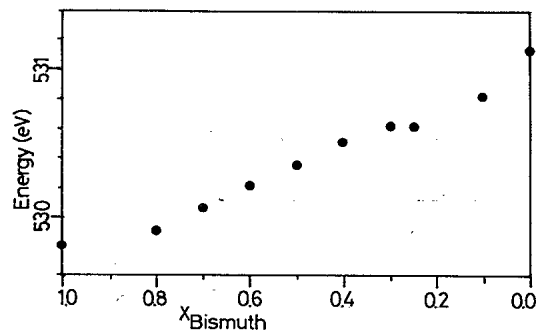

FIG. 4. Maxima of the first peak in the oxygen 1s x-ray-absorption spectra as a function of the bismuth concentration (x_{Bismuth}).

tion of the first peak as a function of the bismuth concentration. A monotonic shift is observed. The discrepancy between calculation and experiment for BaPbO$_3$ precludes a suitable reference point and we cannot fully judge the utility of the different models for treating this problem. Three prominent models are the combined-rigid-band model,[14] the virtual-crystal approximation,[2] and a superlattice calculation.[11] The combined-rigid-band model uses the band-structure results for BaBiO$_3$ and BaPbO$_3$ as input and the density of states of a mixed material is obtained by adding up the densities of states of the pure materials with the Fermi energy shifted to adjust the number of holes (BaBiO$_3$) and electrons (BaPbO$_3$) in-
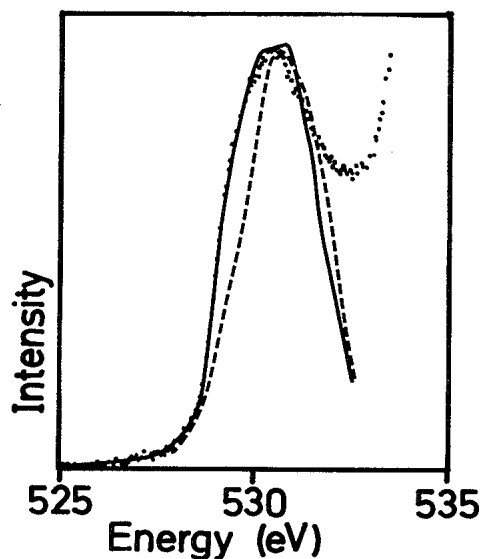

FIG. 5. Comparison of the BaPb$_{0.7}$Bi$_{0.3}$O$_3$ x-ray-absorption result with the broadened oxygen p density of states from Ref. 2 calculated in the virtual crystal approximation for cubic (dashed line) and tetragonal (solid line) crystal structures. The same broadening as in Fig. 3 is applied.

troduced. As the density of states of $BaPbO_3$ is unreliable for our purposes it is not possible to test this model in detail.

Another approach is the calculation of a NaCl superstructure of the lead and bismuth positions for $BaPb_{0.5}Bi_{0.5}$, which can be excluded as the resulting density of states clearly shows a spurious double peak close to the Fermi level,[11] whereas in the experiment there is only one peak, intermediate between the $BaBiO_3$ and $BaPbO_3$ cases. Thus this model seems untenable.

A third model is the virtual crystal approximation.[39] In this model it is assumed that the combination of lead and bismuth atoms can be approximated with an artificial atom with an intermediate nuclear charge. Using this model a calculation has been performed for $BaPb_{0.7}Bi_{0.3}O_3$.[2] Figure 5 compares the broadened oxygen p density of states with the experimental curve. The agreement in shape and position of the first peak is good. Thus like for $BaBiO_3$ ($x_{Bi} = 1$) also for $BaPb_{0.7}Bi_{0.3}O_3$ ($x_{Bi} = 0.3$) there is good agreement in peak position, in contrast to the situation for $BaPbO_3$. Yet, in view of the gross oversimplifications of this model it is not clear what can be concluded from this agreement.

VI. CONCLUDING REMARKS

We have presented an experimental study of the oxygen $1s$ XAS spectra of $BaPb_{1-x}Bi_xO_3$ oxides and have found the following:

(i) No preedge peaks as in the copper-oxide-based superconductors exist and hence there is no evidence for gap states.

(ii) We have found the shifts in the x-ray-absorption spectra to be smaller than predicted by density-of-states calculations. This is a similar result to that found for the *occupied* states by photoemission studies.[20,23-27] We consider the discrepancies for $BaPbO_3$ crucial and they must certainly be cleared up before a proper theoretical understanding of the electronic structure of these materials can be achieved. We suggest that lines of investigation would be to include, one at a time, relativistic effects and core-hole potentials in band-structure calculations in the real crystal structure with a larger energy window in the unoccupied part of the density of states.

(iii) This discrepancy obstructs detailed analysis of the mixing of $BaBiO_3$ and $BaPbO_3$. The experiment shows a smooth trend in the position of the first maximum and a comparison with a virtual crystal calculation at $x_{Bi} = 0.3$ gives satisfactory agreement, suggesting that the discrepancy mainly occurs at the Pb end of the spectrum.

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