

EXAFS OF THE SUPERCONDUCTING OXIDE $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$

A. Balzarotti

Dipartimento di Fisica, Università di Roma II, 00173 Roma, Italy

A.P. Menushenkov

Engineering Physics Institute, 115409 Moscow, U.S.S.R.

N. Motta

Scuola Normale Superiore, 56100 Pisa, Italy

and

J. Purans

Institute of Solid State Physics, Latvian State University, 226063 Riga, Latvia

(Received 15 October 1983 by F. Bassani)

The two-valence state Bi^{3+} and Bi^{5+} of Bi in the semiconductor BaBiO_3 and in the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($x = 0, 0.25, 0.6$ and 1) system has been determined from the EXAFS spectra above the L_{III} -edges of Ba, Pb and Bi. Peaks in the radial distribution function up to 5 \AA from the absorber have been identified through a model calculation using theoretical amplitudes and phase shifts and the interatomic distances from neutron diffraction measurements. We found indication of local disorder in the Pb–Bi sublattice for the mixed compound.

1. INTRODUCTION

SINCE THE DISCOVERY of the superconductivity in the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system [1] the question concerning the valence state of Bi in this compound has taken on great importance. Solid solutions BaPbO_3 – BaBiO_3 have a distorted perovskite-type structure at room temperature which varies from orthorhombic–tetragonal–orthorhombic–monoclinic as a function of increasing x and superconductivity is confined to the tetragonal phase [2].

For many years the question of the oxidation state of Bi in BaBiO_3 [3–5] was unresolved. Lately, independent neutron diffraction studies by Thornton and Jacobson [6] and Cox and Sleight [7] showed that the unit cell of BaBiO_3 is monoclinic and contains four formula units, Fig. 1(a). A striking feature of this structure is that Bi ions occupy two quite distinct sites with average nearest-neighbor oxygens at 2.28 and 2.12 Å , which is consistent with the valence configuration $\text{Ba}_2\text{Bi}^{3+}\text{Bi}^{5+}\text{O}_6$ [7]. The corresponding plot of the thermal ellipsoids of BaBiO_3 is shown in Fig. 1(b). Concerning the mixed compounds $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($x \neq 0, 1$), the valence state configuration of Bi is still an open problem as well as the degree of order of the bismuth–lead sublattices. These issues are relevant to understand the electronic structure [8] and the mechanism of the superconductivity in this material [9, 10].

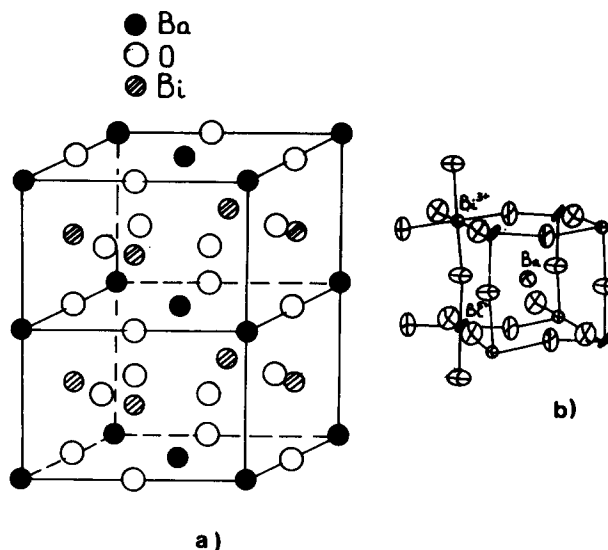


Fig. 1. (a) Double unit cell of the monoclinic distorted perovskite-type structure of BaBiO_3 at $T = 300 \text{ K}$. (b) ORTEP thermal ellipsoids of BaBiO_3 at 419 K showing one octant of the face-centered cell (from [7]).

Since extended X-ray absorption fine structure (EXAFS) gives the local environment and can be superior to X-ray diffraction for structural analysis [11], we used this technique to solve the above problems.

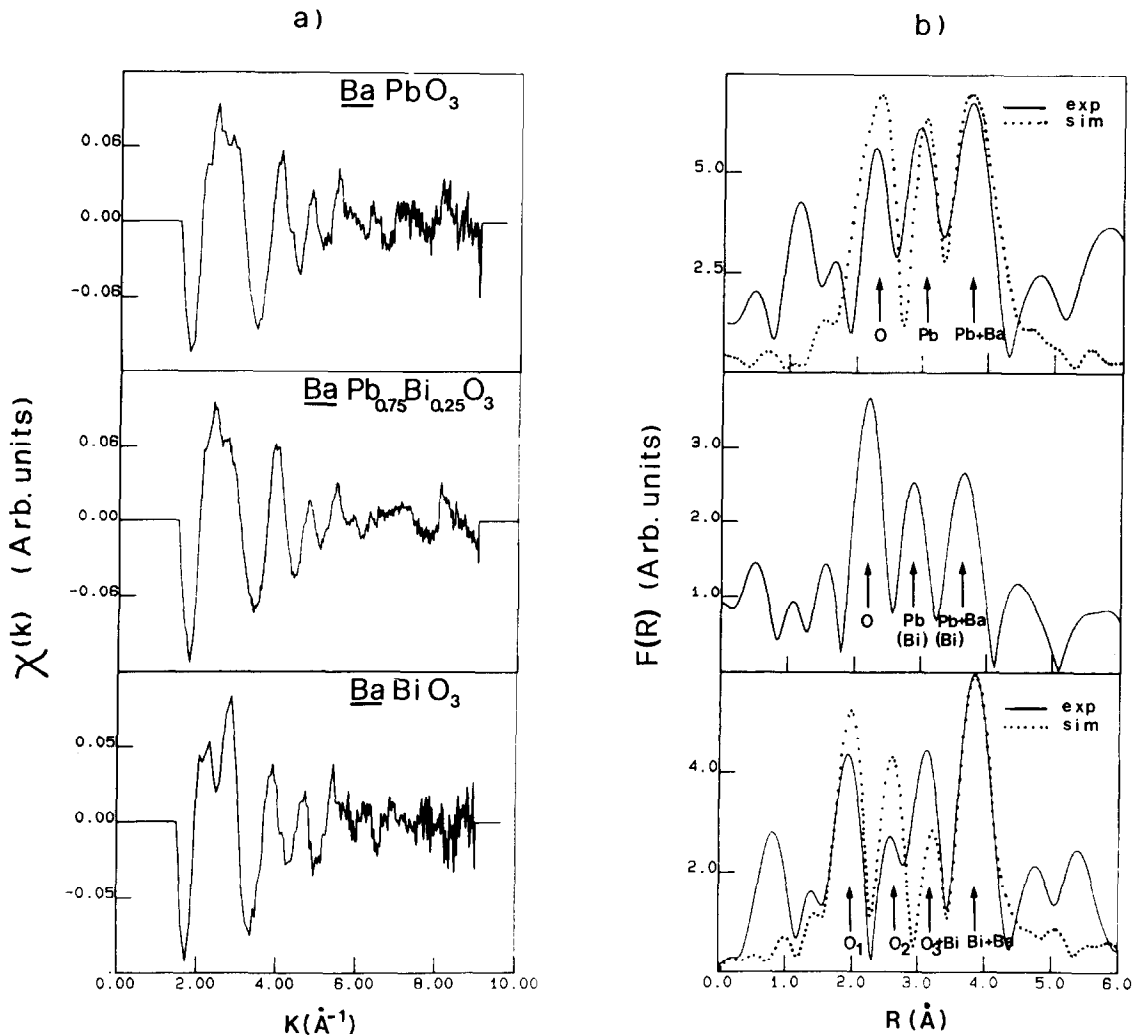


Fig. 2. (a) EXAFS modulation $\chi(k)$ for $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ above the L_{III} -edge of Ba ($x = 0, 0.25$ and 1) at $T = 300$ K. (b) Radial distribution functions obtained from the FT transform of (a) compared with the simulated ones (dotted lines).

From the analysis of the EXAFS spectra above the L_{III} -edges of Ba, Pb and Bi we demonstrate that: (1) oxygen occupies average different positions around Bi which gives clear support to the double valence of Bi in the mixed compound, (2) around each absorber there is no indication of a strong lattice disorder in BaBiO_3 and BaPbO_3 at least up to 5 \AA . However, we find evidence of some disorder in the further ($\sim 4.4 \text{ \AA}$) Pb–Bi shell in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($x = 0.25$ and 0.6).

2. EXPERIMENTAL

The compounds $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ with $x = 0, 0.25, 0.6$ and 1 were prepared in Moscow Engineering Physics Institute by using the conventional ceramic technology [12]. The temperature dependence of the resistivity $\rho(T)$ showed superconducting properties ($T_c \cong 13 \text{ K}$) for $x = 0.25$, typical semiconducting behaviour for

$x = 0.6$ and 1 and semimetallic behaviour for BaPbO_3 . Powders suitable for EXAFS measurements were prepared by mixing $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ with a small amount of HBO_3 . The effective thickness d of the samples was chosen from the condition $1 \leq \mu d \leq 3$, where μ is the atomic absorption coefficient above the interesting core edge. The source of soft X-rays was the storage ring Adone operated at 1.5 GeV and 50 mA . The X-rays were monochromatized by a $\text{Si}(220)$ channel-cut single crystal at about 17 m from the tangent point. Further experimental details have been reported elsewhere [13]. EXAFS spectra were collected above the L_{III} -edges of Ba (5247 eV), Pb ($13,035 \text{ eV}$) and Bi ($13,418 \text{ eV}$). The experimental region scanned – typically 10 \AA^{-1} from each edge – was limited by the occurrence of the Ba L_{II} -edge for Ba, of the Bi L_{III} -edge for Pb and by the maximum photon energy available ($14,500 \text{ eV}$) for Bi. These boundaries set a limit to the

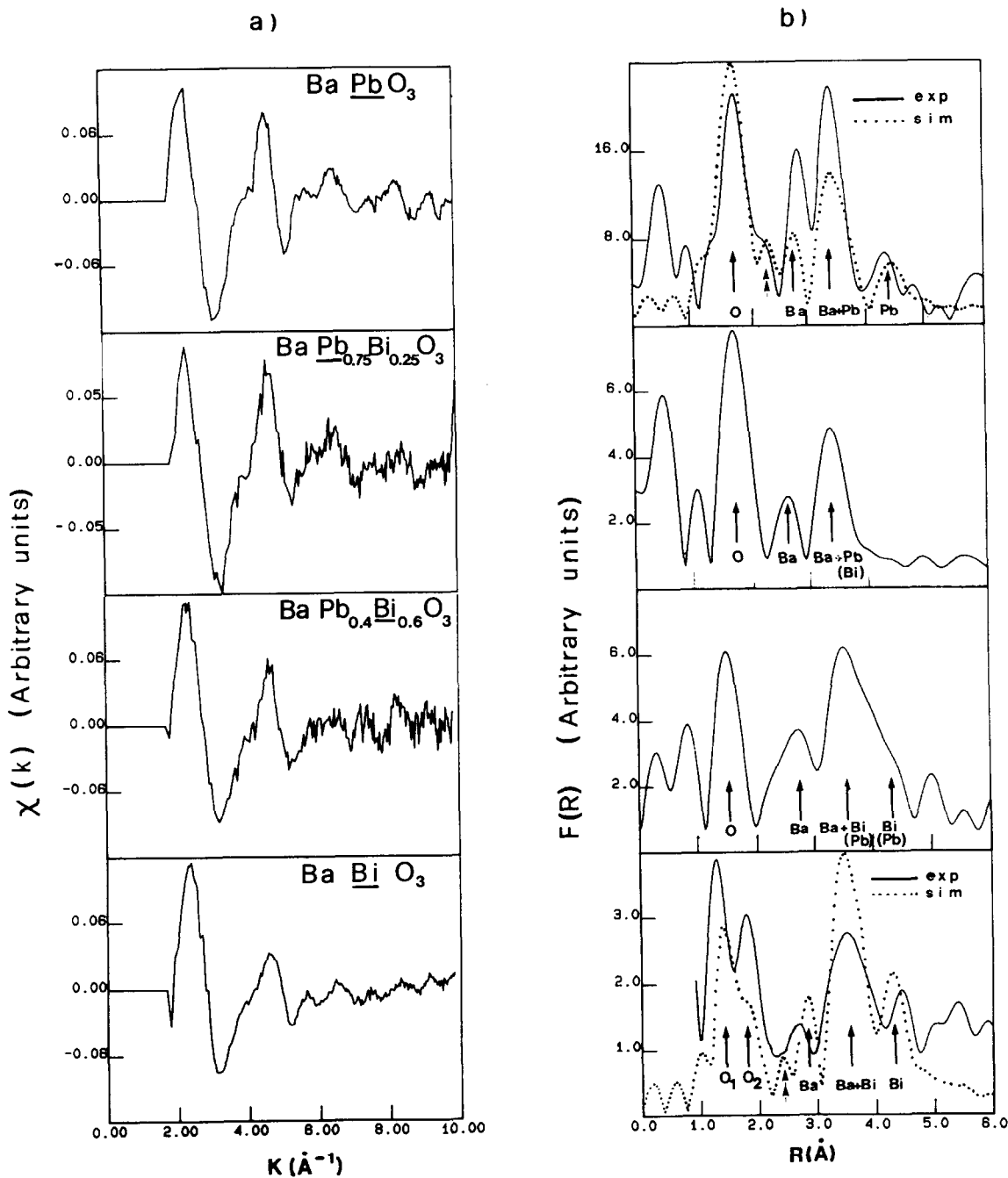


Fig. 3. (a) EXAFS modulation $\chi(k)$ for $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ above the L_{III} -edge of Pb ($x = 0$ and 0.25) and the L_{III} -edge of Bi ($x = 0.6$ and 1) at $T = 300$ K. (b) Radial distribution functions obtained from the FT of (a) compared with the simulated ones (dotted lines).

resolution achievable in the Fourier transform (FT) of the experimental spectra.

3. RESULTS AND DISCUSSION

The measured EXAFS spectra above the L_{III} -edge of Ba and the corresponding radial distribution functions $F(R)$ for $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($x = 0, 0.25$ and 1) are shown

in Figs. 2(a) and 2(b), respectively. To identify the peaks in $F(R)$ we resorted to a model $\chi(k)$ built with amplitudes and phase shifts from Teo and Lee tabulations [14] and interatomic distances from neutron diffraction data [6, 7, 15] for the model compounds BaPbO_3 and BaBiO_3 . For BaPbO_3 the simulated spectrum shows that the first peak arises from O atoms, the second from Pb and the third is due to the superposition

of Ba and Pb shells. The doublet at 2.95 and 3.75 Å is due to the shape of the backscattering amplitude characteristic of the heavy elements [11] and therefore is referred to as a single Ba–Pb distance. Similarly, a single Ba–Bi(Pb) distance is found in BaBiO_3 and $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$. In BaBiO_3 the nearest-neighbor oxygen shell consists of three peaks, which is consistent with the existence of three (or more) inequivalent sites for the oxygen ions in accordance with the two-valence model by Cox and Sleight [4] for $\text{Ba}_2\text{Bi}^{3+}\text{Bi}^{5+}\text{O}_6$.

Additional information is obtained from the analysis of the L_{III} -edges of Pb and Bi, shown in Fig. 3 for compounds with $x = 0, 0.25, 0.6$ and 1. The identification of the FT peaks was made from simulation which showed that the four main peaks in the BaPbO_3 radial distribution function arise from O, Ba, superposition of Ba and Pb, and Pb. The weak structure marked (\dagger) is due to the limited k -region of the FT and to the use of a Hanning window function. Using a Gaussian window such a peak disappears but, as usual, the overall resolution worsens.

In both BaPbO_3 and BaBiO_3 radial distribution functions the fourth peak, which corresponds to the Pb–Bi subshell, is sharp. The substitution of Bi for Pb [see Fig. 3(b) $x = 0.25$] leads to the disappearance of this peak. The same result takes place when Pb substitutes Bi in BaBiO_3 [see Fig. 3(b) $x = 0.6$]. This fact is taken as indicative of some disorder in the Pb–Bi sublattice for the mixed compounds.

The FT of the BaBiO_3 spectrum clearly shows the oxygen peak split into two shells. According to the simulation, the separation of these shells $\Delta R = 0.2$ Å is in good agreement with Cox and Sleight [4] neutron diffraction data. This splitting is additional evidence of the two-valence state of Bi in BaBiO_3 .

For $\text{BaPb}_{0.4}\text{Bi}_{0.6}\text{O}_3$ the first oxygen shell around Bi is unresolved and the corresponding peak of $F(R)$ occurs at a lower distance than the Pb–O peak in $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$. However, the nearly coincidence of the Bi–Ba and Pb–Ba peaks in both these spectra shows that the difference between the phase shifts of Bi and Pb absorbers is negligible. Thus the average distances of the oxygen ions are actually different around Pb and Bi.

Lead enters the lattice substitutionally to bismuth, in Pb^{4+} valence state, as suggested by the fact that the positions of the Pb–O peak coincide in both BaPbO_3 and $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ spectra. Apparently the $\text{Bi}^{3+}(\text{Bi}^{5+})\text{—O}$ bond lengths are modified by Pb so that the oxygen doublet, exhibited by BaBiO_3 , reduces to a single peak at an intermediate distance which differs from the Pb–O distance. This result could indirectly support a double valence state for bismuth in mixed compounds.

4. CONCLUSIONS

We have shown that a detailed analysis of the EXAFS spectra of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ above the L_{III} -edges of Ba, Pb and Bi gives new additional evidence of two-valence state of Bi in BaBiO_3 and in the mixed compounds. It was also found that some disorder exists in the local environment of Pb–Bi sublattices which can, in principle, create local fluctuations of the density of states. This may be important for understanding the mechanism of conductivity and superconductivity in this system.

Further information is contained in the analysis of the X-ray absorption near edge structure (XANES) which will be presented in a separate paper.

Acknowledgements – We thank M. De Crescenzi and S. Mobilio for valuable discussions and Professor E.A. Protasov for providing the samples used in this experiment. Two of us (A.P.M. and J.P.) are indebted to the National Laboratory of Frascati and to the PULS group for the hospitality and the support.

REFERENCES

1. A.W. Sleight, J.L. Gillson & P.E. Bierstedt, *Solid State Commun.* **17**, 27 (1975).
2. D.E. Cox & A.W. Sleight, *Proc. Conf. on Neutron Scattering*, Gatlinburg, Tennessee, 1976, (Edited by R.M. Moon), National Technical Information Service, Springfield (1976).
3. Y. Khan, K. Nahm, M. Rosenberg & H. Willner, *Phys. Status Solidi (a)* **39**, 79 (1977).
4. D.E. Cox & A.W. Sleight, *Solid State Commun.* **19**, 969 (1976).
5. J.Th.W. De Hair & G. Blasse, *Solid State Commun.* **12**, 727 (1973).
6. G. Thornton & A.J. Jacobson, *Acta Cryst.* **B34**, 351 (1978).
7. D.E. Cox & A.W. Sleight, *Acta Cryst.* **B35**, 1 (1979).
8. L.F. Mattheiss & D.R. Hamann, *Phys. Rev.* **B26**, 2686 (1982).
9. T.M. Rice & L. Sneddon, *Phys. Rev. Lett.* **47**, 689 (1981).
10. A. Alexandrov & J. Ranninger, *Phys. Rev.* **B24**, 1164 (1981).
11. P.A. Lee, P.H. Citrin, P. Eisenberger & B.M. Kincaid, *Rev. Mod. Phys.* **53**, 769 (1981); T.M. Hayes & J.B. Boyce, *Solid State Phys.* **37**, 17 (1982).
12. A.P. Menushenkov, E.A. Protasov & E.V. Chubunova, *Fiz. Tverd. Tela (Leningrad)* **23**, 3703 (1981); *Sov. Phys. – Solid State* **23**, 2153 (1981).
13. A. Balzarotti, M. De Crescenzi & L. Incoccia, *Phys. Rev.* **B25**, 6349 (1982).
14. B.K. Teo & P.A. Lee, *J. Am. Chem. Soc.* **101**, 2815 (1979).
15. G. Thornton & A.J. Jacobson, *Mat. Res. Bull.* **11**, 837 (1976).