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An EXAFS Study of the Luminescent Bi^{3+} Center in $LaPO_4$–Bi

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In order to determine the oxygen coordination of the Bi^{3+} ion in $LaPO_4$–Bi, extended X-ray absorption fine structure (EXAFS) spectra were measured of $BiPO_4$ and $LaPO_4$–Bi. Analysis of the EXAFS data shows that the Bi^{3+} ion in $LaPO_4$–Bi occupies the La^{3+} site, but that the oxygen coordination of the Bi^{3+} ion is distorted relative to that of La^{3+} in undoped $LaPO_4$. The oxygen coordination shows a resemblance to that of Bi^{3+} in $BiPO_4$. The importance of these results for the Bi^{3+} luminescence is discussed.

1. Introduction

The luminescence of Bi^{3+} in solid mixed-metal oxides is well known and its characteristics have been shown to vary strongly from lattice to lattice (*1*, *2*). The variation of the Stokes shift with more than a factor of 10 is especially impressive and intriguing (*3*, *4*). It has been proposed that this variation can be related to the $6s^2$ electronic configuration of the Bi^{3+} ion which tends to induce a very asymmetrical coordination (*4*).

Small Stokes shifts were observed for Bi^{3+} in very constrained surroundings in which case it is assumed that there is no space for changes in coordination relative to the unsubstituted situation. This is especially observed if the Bi^{3+} ion is substituted for smaller ions (e.g., Sc^{3+}, Lu^{3+}, Y^{3+}) on six-coordinated sites (*1*, *2*).

Large Stokes shifts are observed for Bi^{3+} which is substituted for larger ions on less constrained sites, e.g., Bi^{3+} in $LaPO_4$ (with an oxygen coordination of eight or nine for La^{3+} (*3*, *5–8*)), or Bi^{3+} in bismuth compounds like $Bi_3Ge_4O_{12}$ (*1*, *2*, *4*, *9*) and $Bi_2Ge_3O_9$ (*1*, *2*, *4*, *10*). In the latter compounds X-ray diffraction studies have shown that Bi^{3+} is asymmetrically coordinated. In fact, asymmetrically coordinated Bi^{3+} ions always exhibit broadband emission with a large Stokes shift. Therefore, it has been assumed that the Bi^{3+} ion is also asymmetrically coordinated in $LaPO_4$, or more generally, that broadband emission with a large Stokes shift indicates that the Bi^{3+} ion has a coordination which has been adjusted to the $6s^2$ configuration.

However, there is no direct proof for this assumption. Actually, it is rather difficult to determine directly the position of the oxygen ions surrounding a small amount of Bi^{3+} ions in a host lattice. EXAFS (extended

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X-ray absorption fine structure) is a suitable tool to obtain information about the immediate surroundings of the Bi^{3+} ion substituted in a given lattice. This paper reports the results of such a study. As the sample to be studied we selected $LaPO_4$–Bi (*5*). The Stokes shift of the Bi^{3+} emission is high, viz. about 19,000 cm^{-1}, so that possible changes in the coordination must be most outspoken in this case.

2. Experimental

$LaPO_4$–Bi and $BiPO_4$ were prepared as described in the literature using solid state reactions (*5*). $BaPbO_3$ was prepared, according to (*11*). All samples were checked by Cu$K\alpha$ radiation. Both $BiPO_4$ and $LaPO_4$–Bi appeared as monazite (*12*). The Bi concentration in $LaPO_4$–Bi amounts to 5%.

The EXAFS experiments were carried out at Wiggler station 9.2 at the Synchrotron Radiation Source (SRS) in Daresbury, United Kingdom, with a ring energy of 2 GeV and a ring current between 100 and 280 mA. A Si(220) double crystal monochromator (d = 1.92 Å) which had been detuned (to 50% of the maximum radiation intensity) in order to reduce higher harmonic contributions was employed. The powdered samples were pressed into self-supporting wafers to give samples of good uniformity. The wafer thickness was chosen to give a total X-ray absorbance of about 2.5. The experiments were carried out in an evacuated *in situ* EXAFS cell at liquid nitrogen temperature. $LaPO_4$–Bi and $BiPO_4$ were measured at the Bi L_{III}-edge (13,426 eV). As $BiPO_4$ and $LaPO_4$ both belong to the monazite class of compounds, with lattice parameters differing less than 1.5% (*6*), it was hoped that effects caused by the substitution of Bi^{3+} in $LaPO_4$ would show as differences between the $BiPO_4$ and the $LaPO_4$–Bi EXAFS spectra. $BaPbO_3$, which was considered to be a good reference compound for Bi–O contributions, was measured at the Pb L_{III}-edge (13,055 eV).

3. Results

The raw EXAFS data (with a high signal-to-noise ratio) for $LaPO_4$–Bi and $BiPO_4$ are shown in Figs. 1a and 1b, respectively. The data were obtained from the X-ray absorption spectrum by a cubic spline background subtraction (*13*), followed by normalization by division by the edge height (*14*). The EXAFS data for $BaPbO_3$ were obtained in the same way.

$BaPbO_3$ was used as a reference compound to obtain the phase and backscattering amplitude functions for the Pb–O pair. In $BaPbO_3$ the Pb^{4+} ion is surrounded by six oxygen ions, two at 2.145 Å and four at 2.150 Å, forming a very slightly distorted octahedron (*11*). Bismuth compounds in which the first metal–oxygen shell is so ideal (symmetrical arrangement, small spread in metal–oxygen distances) cannot be found. Generally, Bi–O coordination shells tend to consist of a broad range of Bi–O distances, which makes it difficult to obtain good phase and backscattering amplitude functions for the Bi–O pair. However, it has been shown both theoretically (*15*) and experimentally (*16*, *17*) that the phase and backscattering amplitude for a certain absorber–scatterer pair can also be used for other pairs in which the absorber atom is a neighbor in the periodic table. Therefore we have used the first Pb–O shell in $BaPbO_3$ as a reference for Bi–O contributions. Table I gives the crystallographic data of the first Pb–O shell in $BaPbO_3$, and the forward and inverse Fourier transformation ranges used to isolate the contributions of this shell.

The imaginary part and magnitude of the k^1-weighted Fourier transform of the $LaPO_4$–Bi and $BiPO_4$ data are shown in Figs. 1c and 1d. The Fourier transforms are

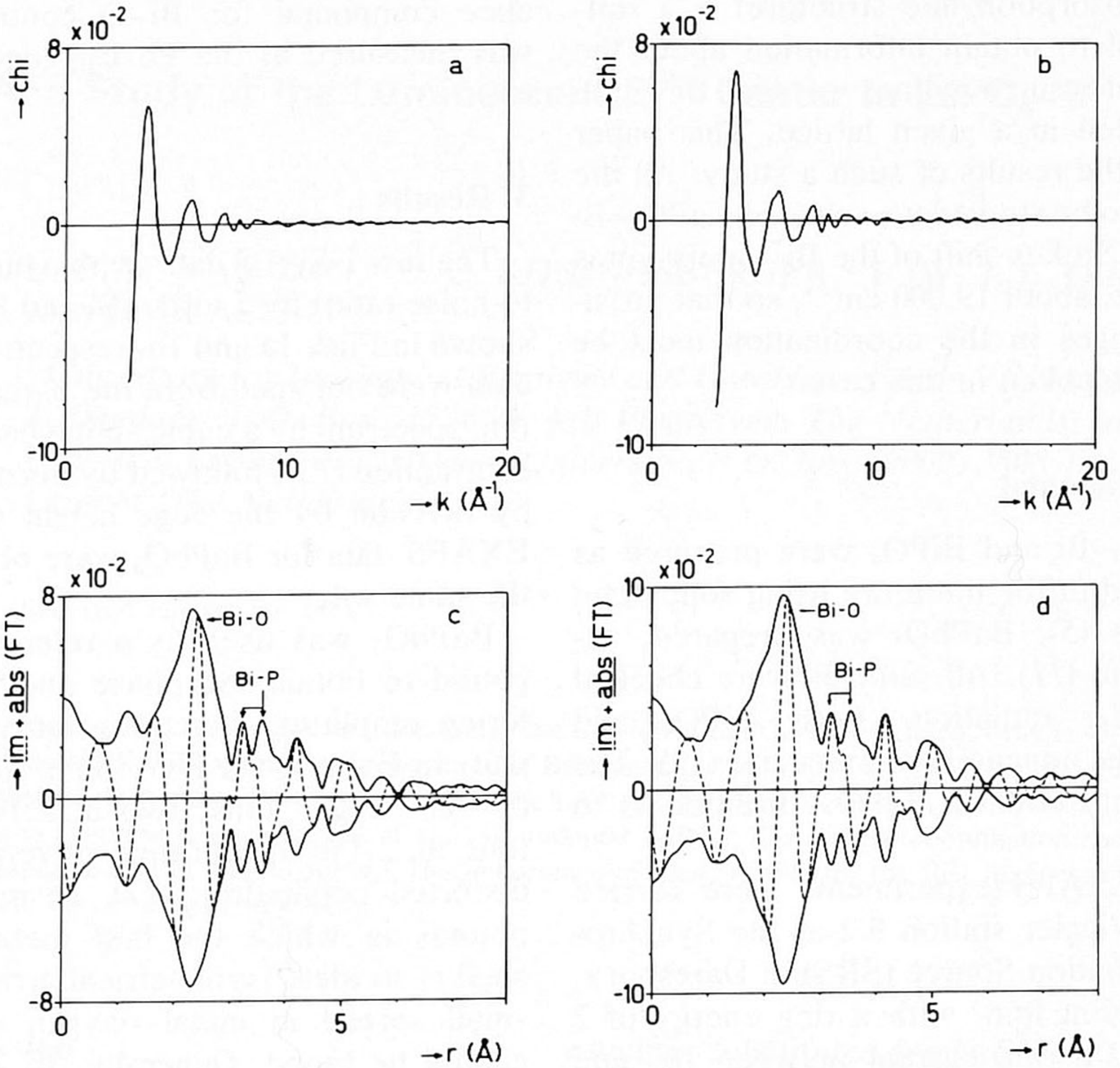

FIG. 1. Raw EXAFS data for $LaPO_4$–Bi (a) and $BiPO_4$ (b); k^1-weighted Fourier transforms (Δk = 3.2–13.9 Å^{-1}, Bi–O phase corrected) for $LaPO_4$–Bi (c) and $BiPO_4$ (d); (––) imaginary part, (—) magnitude.

TABLE I

FOURIER TRANSFORMATION RANGES USED IN THE ISOLATION OF THE FIRST METAL–OXYGEN SHELL IN $BaPbO_3$, $LaPO_4$–Bi, AND $BiPO_4$ AND THE STRUCTURAL PARAMETERS OBTAINED FOR THESE SHELLS BY X-RAY DIFFRACTION AND EXAFS

Sample	k^n	FT (Å^{-1})	FT^{-1} (Å)	N	R (Å)	$\Delta\sigma^2$ (Å^2)[c]	V_0 (eV)[c]
$BaPbO_3$	k^3	2.47–16.37	0.56–2.14	6[a]	2.148[a]	0	0
$LaPO_4$–Bi	k^1	3.24–13.94	0.40–3.10	8[a]	2.390[b]	0.017[b]	−2.4[b]
$BiPO_4$	k^1	3.23–13.97	0.40–3.06	8[a]	2.385[b]	0.012[b]	−0.7[b]

Note. N, coordination number; R, coordination distance; $\Delta\sigma^2$, Debye–Waller factor; V_0, inner potential correction.

[a] By X-ray diffraction.

[b] By EXAFS. EXAFS accuracies: $R \pm 0.02$ Å, $\Delta\sigma^2 \pm 0.001$ Å^2.

[c] With respect to the first Pb–O shell in $BaPbO_3$ (*11*).

corrected for the Bi–O phase shift. If single Bi–O shells are present, the Bi–O phase corrected Fourier transform should show them as peaks at the proper Bi–O distances, in which the imaginary part peaks positively (*14*, *18*).

Below 3.9 Å, the spectra are very much alike. However, significant difference in peak intensity can be observed at approximately 2.4 Å. Also differences in phase and intensity are observed around 4.5 Å. A single Bi–O peak appears for each sample at approximately 2.4 Å. This is a surprising result, because it is known that the first metal–oxygen shell in both phosphates consists of a rather broad range of metal–oxygen distances (*6–8*, *12*). We concluded that in this case, the differences in the Bi–O coordination distances were nevertheless small enough to allow the shell to be treated as a single distance shell with a large Debye–Waller factor, mainly due to structural disorder.

An inverse Fourier transformation was applied to both Bi spectra in order to isolate the first shell Bi–O contributions. The ranges used in the forward and inverse Fourier transformations are given in Table I. The isolated Bi–O shells were fitted with a single shell model, using the Bi–O phase and backscattering amplitude derived from $BaPbO_3$. In this fitting procedure the number of oxygen neighbors N was kept constant to eight, as determined by X-ray diffraction for $BiPO_4$ (*6*). In this way, for both $LaPO_4$–Bi and $BiPO_4$ good fits were obtained which differed mainly in the figure obtained for the Debye–Waller factor (with respect to $BaPbO_3$). As the accuracy of N in the EXAFS analysis amounts to 10–15%, it may also be possible that there are nine oxygen neighbors in the first metal–oxygen coordination shell, as has been reported for $LaPO_4$ (*7*, *8*). The best-fit parameters are given in Table I. In Figs. 2a and 2b the imaginary part of the Fourier transform of the isolated Bi–O shell and that of the best fit are shown for $LaPO_4$–Bi and $BiPO_4$, respectively. The Bi–O contributions calculated on the basis of the best-fit parameters were subsequently subtracted from the proper EXAFS data. The imaginary part and magnitude of the Fourier transformation of the difference spectra are shown in Figs. 2c and 2d for $LaPO_4$–Bi and $BiPO_4$. No significant peaks are observed at the position of the first Bi–O shell. The peak which appears in both spectra at 1.2 Å is caused by background signal that could not be fully eliminated. A 1.2-Å distance is far too small for a real Bi–O coordination distance.

However, there is significant structure present above $r = 3$ Å. From X-ray diffraction results it is known that Bi–Bi and Bi–La contributions should be present above $r = 3.9$ Å (*6–8*). A large difference is observed here between the two spectra, caused by the different X-ray scattering behavior of La with respect to Bi. Between $r = 3$ and 3.9 Å mainly contributions from Bi–P shells are expected. In this range two distinct peaks of which the magnitude and imaginary part are equal for both spectra, are observed. This similarity in the Bi–P shells of $BiPO_4$ and $LaPO_4$–Bi was not expected after the observed difference in the Bi–O shell. The large disorder difference in the first Bi–O shell clearly does not extend to the higher coordination shells.

4. Discussion

EXAFS Results

The strong increase in the value for the Debye–Waller factor of the first Bi–O shell in $LaPO_4$–Bi with respect to $BiPO_4$ is the most outspoken difference in the EXAFS analysis of both samples. We presume that this is mainly caused by increased structural disorder of the nearest neighbor oxygen atoms around the Bi^{3+} ions in $LaPO_4$–Bi. This is strongly supported by the fact

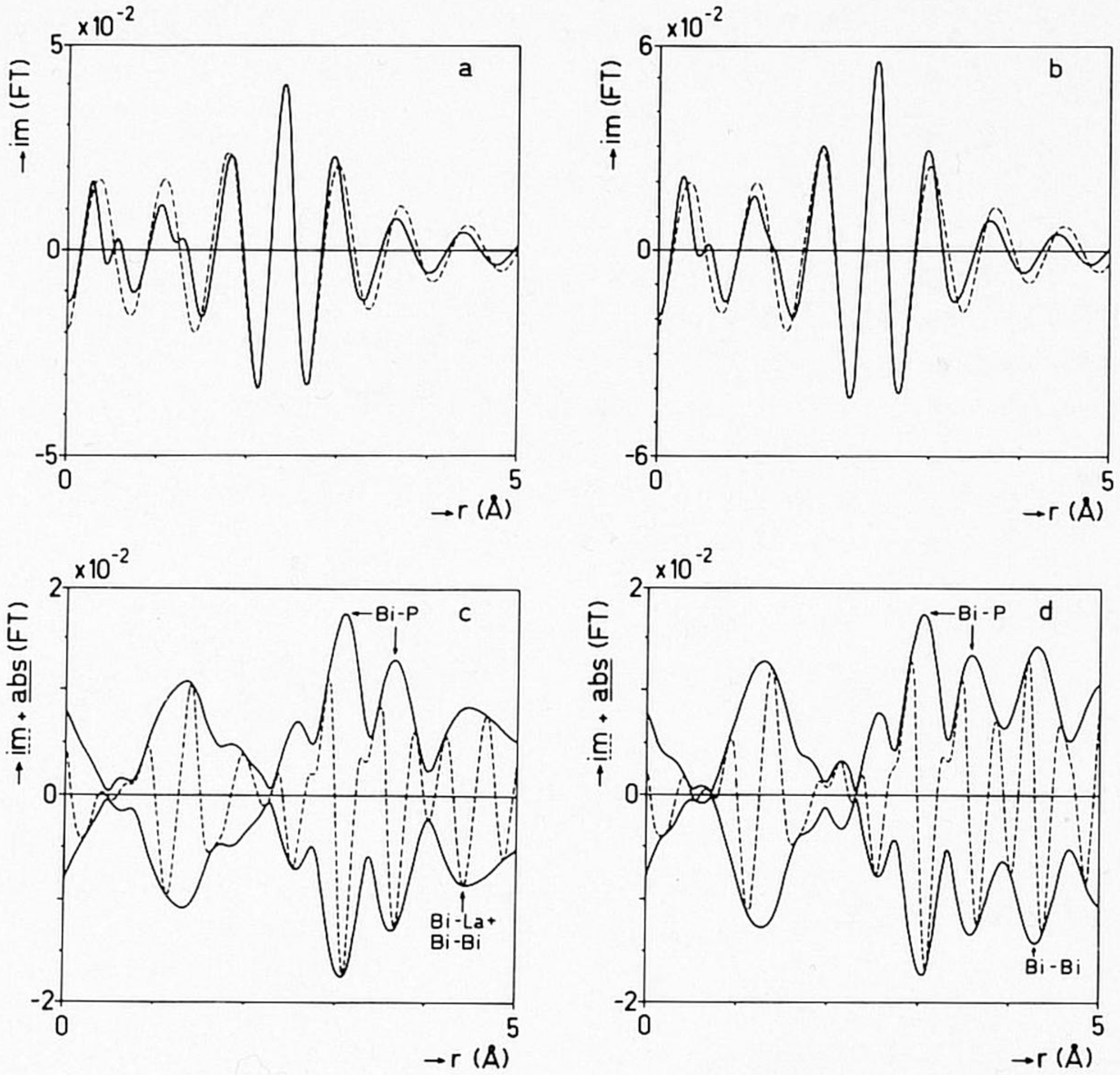

FIG. 2. Imaginary part of k^1-weighted Fourier transforms (Δk = 4.3–13.1 Å^{-1}, Bi–O phase corrected) of (—) isolated first Bi–O shell and (– – –) calculated Bi–O shell on the basis of best-fit parameters (see Table I) for $LaPO_4$–Bi (a) and $BiPO_4$ (b); k^1-weighted Fourier transforms (Δk = 4.4–12.7 Å^{-1}, Bi–O phase corrected) of the difference between experimental data and calculated Bi–O shell for $LaPO_4$–Bi (c) and $BiPO_4$ (d); (– – –) imaginary part, (—) magnitude.

that a negligible difference in disorder is observed for the next Bi–P shells. If an increase in intrinsic thermal disorder is expected to be the main cause of the observed difference in the Bi–O shell, then surely this should also affect the Bi–P shells.

Regarding the large difference in disorder, it should be possible to obtain a better picture of the structural differences in the Bi–O shell by splitting it into several subshells. However, a straightforward multiple-shell fit is not reliable in this case, because the number of parameters that can be fitted agreeably is restricted by (i) the relatively small range in r space in which the subshells should occur, and (ii) the low reliability of Bi–O data at high k values. As a result it appears that hardly a two-shell fit is reliable under the circumstances.

Therefore we have chosen to perform three-shell model calculations, in which it was tried to mimic the Bi–O peak form in r space as closely as possible (taking into account the imaginary part as well as the magnitude). To reduce the number of degrees of freedom, inner potential corrections were not applied. Further, the number of oxygen atoms in each subshell was chosen to resemble X-ray diffraction structures reported for the monazites (*7*, *8*, *19*). The total number of oxygen atoms was

still kept equal to eight, because in most structure reports the ninth oxygen atom is somewhat farther removed from the central metal ion (*7*, *19*). In the first step of the model calculations, the four oxygen atoms of the middle-distance subshell were positioned at 2.39 Å, the coordination distance that had been obtained in the fit procedure. The Debye–Waller factor was then adjusted until in r space no distinct peak at 2.39 Å was observed in the difference spectrum (experimental data minus calculated Bi–O shell). Subsequently the coordination distance and Debye–Waller factor were chosen for the oxygen atom in the short-distance subshell, and it was tried to obtain a good coincidence of this calculated peak and the difference spectrum between 2.0 and 2.3 Å. Finally, both the short- and middle-distance subshell spectra were subtracted from the experimental data and the peak between 2.4 and 2.7 Å in the resulting difference spectrum was mimicked as closely as possible by varying the coordination distance and Debye–Waller factor for the three oxygen atoms in the long-distance subshell. The three calculated Bi–O contributions were then added and compared with the experimental data in r space. If differences were observed, both the short- and long-distance subshells were subtracted from the experimental data, and values for the coordination distance and Debye–Waller factor of the middle-distance subshell that yielded better coincidence with the peak at approximately 2.4 Å in r space in the difference spectrum were selected. The entire procedure was repeated until the best possible coincidence of the experimental data and the three calculated subshells was obtained in r space. With this procedure it was possible to obtain a good resemblance in r space. In fact, for $LaPO_4$–Bi as well as for $BiPO_4$ the best results with one (fitted) shell or three (calculated) shells agreed well, and no significant features could be observed when the difference spectra obtained via the two methods were compared. The parameters used in the model calculations are given in Table II.

When the Bi–O coordination distances for $LaPO_4$–Bi and $BiPO_4$ in Table II (obtained by EXAFS) are compared with those reported from X-ray diffraction for $BiPO_4$ and $LaPO_4$ (*6–8*), it is obvious that the smallest metal–oxygen coordination distance obtained with EXAFS (approximately 2.2 Å) is much smaller than that reported with X-ray diffraction (2.3–2.4 Å). Model calculations in which the metal–oxygen distances from the X-ray diffraction structure of $LaPO_4$ (*7*, *8*) are used do not reproduce the first Bi–O peak of $LaPO_4$–Bi very well, especially at the low r side of the peak. Also, model calculations on the basis of the X-ray diffraction structure of $BiPO_4$ (*6*) do not agree at all with the experimental EXAFS data of $BiPO_4$. As these X-ray diffraction results are rather old (1962, (*6*)), and their accuracy for the oxygen positions is low, it is assumed that in reality shorter Bi–O distances than those reported exist. For example, for α-Bi_2O_3 more recent X-ray diffraction studies have yielded shorter Bi–O distances and more disorder in the first Bi–O shell (*20*, *21*) which is in line with the differences observed between EXAFS and the old X-ray diffraction results for $BiPO_4$. Also for the high-temperature modification of $BiPO_4$, which is related to the monazite modification, one Bi–O coordination at short distance (2.15 Å) has

TABLE II

STRUCTURAL PARAMETERS USED TO DESCRIBE THE FIRST Bi–O SHELL IN $LaPO_4$–Bi AND $BiPO_4$ BY THREE SUBSHELLS

			$LaPO_4$–Bi		$BiPO_4$	
Shell	N	V_0 (eV)[a]	R (Å)	$\Delta\sigma^2$ (Å^2)[a]	R (Å)	$\Delta\sigma^2$ (Å^2)[a]
1	1	0	2.19	0.0035	2.21	0.0020
2	4	0	2.34	0.0033	2.358	0.0017
3	3	0	2.49	0.0045	2.49	0.0046

Note. N, coordination number; R, coordination distance; $\Delta\sigma^2$, Debye–Waller factor, V_0, inner potential correction.

[a] With respect to the first Pb–O shell in $BaPbO_3$ (*11*).

been observed with XRD (*22*). However, it is clear from the calculated results that Bi^{3+} in $BiPO_4$ and $LaPO_4$–Bi is coordinated by oxygen in a similar way. It seems that only the most nearby oxygen subshells in La PO_4–Bi are more disordered and perhaps somewhat displaced with respect to $BiPO_4$.

The EXAFS Results in Relation to the Bi^{3+} Luminescence

It is clear that the EXAFS technique cannot yield the exact coordination of the Bi^{3+} ion in $LaPO_4$–Bi. Nevertheless it is possible to draw some important conclusions.

The introduction of Bi^{3+} in $LaPO_4$ clearly changes the position of the nearest oxygen ions. The range in distances in the first Bi–O coordination shell of $LaPO_4$–Bi as obtained by EXAFS differs considerably from the relatively recent results that are reported with X-ray diffraction for the first La–O shell, viz., 2.40–2.81 Å (*7*) and 2.31–2.97 Å (*8*), while the EXAFS results for $LaPO_4$–Bi and $BiPO_4$ are very similar.

It is obvious that, although a strong structural similarity exists between $LaPO_4$ and $BiPO_4$, the first metal–oxygen coordination shells in these phosphates are not equal at all. It seems that when Bi^{3+} is substituted in $LaPO_4$, Bi^{3+} induces displacement of the most nearby oxygen ions toward positions occurring in $BiPO_4$. The influence of the host lattice shows as more disorder in the shortest Bi–O coordination distances with respect to $BiPO_4$. Also, these shortest Bi–O distances might be slightly different in $BiPO_4$ and $LaPO_4$–Bi. This observed structural change confirms the model presented by us before (*1*, *2*, *4*) in a direct way.

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