Local Electronic Structure of PbVO$_3$, a New Member of PbTiO$_3$ Family, studied by XANES/ELNES

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Abstract
Recently an interesting multi-ferroic system PbVO$_3$ [Chem. Mater. 2004] was successfully prepared using a high-pressure and high-temperature technique. The crystallographic features were reported. In this note we concentrate on the theoretical XANES spectra by considering the K-edge of Vanadium. The tetragonality [c/a=1.229 at 300 K] of PbVO$_3$ is the largest in the PbTiO$_3$ family of compounds. Thus one is led naturally to examine the effect of the change of tetragonality and the axial oxygen position on the electronic structure [i.e. XANES spectrum]. We study this effect in two ways. At a given temperature we vary the tetragonality and the axial oxygen position and quantify it in terms of XANES difference spectrum. Secondly, we compute the XANES spectra at three different temperatures, 90 K, 300 K, and 530 K and quantify the change in terms of the difference spectrum. We note that in this compound the tetragonality increases almost monotonically with temperature from 12 K to 570 K without transition to the cubic phase under ambient pressure. A key objective of the current investigation is to gain an understanding of various absorption features in the vicinity of K-edge of V, in terms of valence, local site symmetry, local coordination geometry, local bond distances, charge transfer, and local projected density of states. We consider both the polarized and the unpolarized XANES spectra. In short we have performed a local electronic study, which nicely complements the crystallographic features reported recently in PbVO$_3$.

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1 Introduction

Using high-pressure and high-temperature techniques, PbVO$_3$ has been synthesized by Belik et al. [1], and Shpanchenko et al. [2].

One of the most interesting features of PbVO$_3$ is its large tetragonality [c/a=1.229 at 300 K] in comparison to that of PbTiO$_3$ [c/a=1.064 at 300 K]. The large tetragonal distortion implies that it will have also a sizable polarization, $P_s$. Indeed a rough calculation [1] employing the ionic model gives a value close to 100 $\mu$C/cm$^2$. This is to be compared to $P_s$=81 $\mu$C/cm$^2$ at 300 K for PbTiO$_3$, $P_s$=26 $\mu$C/cm$^2$ at 300 K for BaTiO$_3$, and $P_s$=37 $\mu$C/cm$^2$ at 543 K for KNbO$_3$, in the same family of compounds. It is well-known and reasonable to expect that ferroelectricity in ionic crystals is correlated with crystal structure distortion. The basic reason is simple, polarization is directly caused by the atomic displacement. A very well-known example is PbTiO$_3$, a perovskite-type tetragonal crystal structure, space group P4mm at 300 K and a simple cubic structure above 763 K. More interesting is the phenomenon, when a material exhibits two or all three of the properties of (anti)ferroelectricity, (anti)ferromagnetism, and (anti)ferroelasticity. These materials are called multiferroics, a recent example is BiFeO$_3$ which exhibits a PbTiO$_3$-type structure. Other examples are YMnO$_3$, BiMnO$_3$, TbMnO$_3$, and TbMn$_2$O$_5$. It is clear that these materials contain a magnetic transition metal ion [such as Mn, Fe] in conjunction with Bi$^{3+}$ and Pb$^{2+}$.

It is well-known that as the region close to the x-ray near edge is scanned in energy, the ejected photoelectron sequentially probes the unoccupied electronic levels of materials. This results in a fine x-ray absorption near edge structure [XANES], within roughly 30-50 eV of the threshold. XANES thus contains useful chemical and structural information.

The main point is that this region is dominated by strong photoelectron scattering. Thus it is highly non-trivial to develop a code to take into account the multiple scattering which dominate the XANES region. Perhaps one of the most elegant XANES code is the FEFF8 series[3, 4]. This ab initio based on the real-space multiple scattering [RSMS] and one of its several advantages is that it applies to both periodic and aperiodic systems.

Thus the purpose of this note is to concentrate on the theoretical calculation using the updated version of FEFF8, i.e. FEFF8.20 [4], for the PbVO$_3$, using the crystallographic data reported recently by one of us [1]. In particular we calculate the near edge spectra of this system for several cases of interest. In addition we also study the near-edge structure for the in-plane and out of plane cases.

Here we report on our results of PbVO$_3$, for the P4mm phase. The calculated XANES spectra are remarkably self-consistent. We have performed several cross-checks in addition to the Self-Consistent-Field [SCF] cycles used in FEFF8 to obtain high level accuracy. It is to be noted that the calculations are based on SCF one-electron Green’s function approach, where many-body effects are taken into account in terms of final-state potentials and a complex energy-dependent self-energy. In this scattering theoretic approach the structure in XANES is correlated with projected density of states [pDOS].
Another aim is to provide a concrete example of the application of XANES and DOS calculations using FEFF. Indeed, although FEFF is a powerful code, its self-consistency must be demonstrated by applications to real systems systematically. Moreover by actual calculations one can illustrate advantages and disadvantages, and thus find ways of improving the code.

This paper is organized as follows, in the next section we outline some basic points about the multiple scattering calculations based on the FEFF8 code. In section three the results and discussion of our study of PbVO$_3$ are given using the FEFF8 code. The final section contains the conclusions.

2 Multiple Scattering via FEFF8

It is well-known that XANES refers to roughly the 40-50 eV region near the edge of X-ray absorption spectroscopy [XAS]. The main point is that this region is dominated by strong photoelectron scattering. Thus it is highly non-trivial to develop a code to take into account the multiple scattering which dominate the XANES region. Perhaps one of the most elegant XANES code is the FEFF8 series[3, 4]. This ab initio based on the real-space multiple scattering [RSMS] and one of its several advantages is that it applies to both periodic and aperiodic systems. In this approach the self-consistent field [SCF] calculations for both the local electronic structure and x-ray absorption spectra are implemented. It is important to note that the full-multiple scattering [FMS] is taken into account for a “small cluster” of atoms plus the higher-order multiple scattering from scatterers outside the said cluster. Some of its main advantages are: SCF estimate of Fermi energy, orbital occupancy and charge transfer.

In this note we concentrate mainly on giving the $\mu(E)$ and the difference $\mu(E)$ spectra. The value $\mu(E)$ is the main quantity in XANES. Here we look at the basic definitions restricting ourselves to brief comments. As is well-known the primary quantities with which XANES calculations are concerned are $\mu, \mu_0, \chi$, and $\rho_{li}(E)$[3]

$$\mu_{li}(E) = \mu_{li}^0(E)[1 + \chi_{li}(E)].$$  

(1)

We note that the prime is here for clarity since it reminds us that it denotes final state quantities in the in the presence of screened hole. The central quantity in X-ray Absorption Spectroscopy [XAS] is the absorption coefficient $\mu(E)$. As is known there is a close and deep connection between XAS and electronic structure, which is indicated and implied by the resemblance of the contribution from a site, $i$ and orbital angular momentum $l$ and the local $l$-projected electronic density of states [LDOS] at site $i$

$$\rho_{li}(E) = \rho_{li}^0(E)[1 + \chi_{li}(E)].$$  

(2)

We provide, a concrete example of this inter-relationship between absorption and LDOS in Fig. 4. It is clear that the main features or peaks of the two quantities, absorption and LDOS
strongly resemble each other, as they should. Incidentally, this provides an independent check on our calculation.

However, it is important to bear in mind that since core hole plays a significant role in calculation of XAS, the similarity between XAS and LDOS cannot be regarded as an absolute.

It is important to keep in mind that FEFF method starts from the most fundamental quantity i.e. the Real Space Green’s Function and constructs the physical quantities of interest from it [3, 4]. This is one of the code’s main attractions since unlike band calculations it does not depend on symmetry. In this sense it is ideal for cluster physics\(^1\). In the shorthand notation the MS expansion can be written as [3]

\[
G^{SC} = G^0 t G^0 + G^0 t G^0 t G^0 + G^0 t G^0 t G^0 t G^0 + ..., \tag{3}
\]

where \(G^{SC}\) represents the self-consistent Green’s Function and \(t\) the scattering \(t\) matrix. It is clear that in FMS we can implicitly sum Eq.(3) to all orders by using matrix inversion, i.e.

\[
G^{SC} = G^0 (1 - t G^0)^{-1}, \tag{4}
\]

as it follows simply from the form of Eq.(3).

3 Results and Discussion

Let us now give the results and analysis of our calculated theoretical results using FEFF8.20. The major input we use is the crystallographic and positional information refinements recently given by one of us [1]. This information is available at 90 K, 300 K and 570 K and for convenience is listed in Table I.

For the purposes of this note we consider the XANES results, where we consider all the atoms up to the distance of 7 Å, from the central or core atom, i.e. V. The exact enumeration is given in Table II for the case, when the temperature is 90 K. The distances from V are calculated with Atoms [version 3.0beta10] program [5]. A total of 110 atoms including the central atom are included in the current XANES calculation, Table II. The shell and atom number for temperatures 300 K and 530 K are respectively given in Tables III and IV. From Tables II-IV, several points are immediately clear. We can clearly see that V atom is five-fold coordinated, with axial oxygen atoms asymmetrically situated. In other words, there is a very strong octahedral distortion with one very short Vanadyl V-O distance. Thus the axial oxygen distances in PbVO\(_3\) are much further apart compared to PbTiO\(_3\). This information is summarized as a comparison of PbVO\(_3\) and PbTiO\(_3\) in Table V. The oxidation state of the five-fold coordinated V can be readily be estimated by using the relation \(Z = 25.99 - 11.11 l_{V - OP}[x]\) and the value of \(V - OP = 1.98583\) Å from Table V,

\(^1\)It is known that XANES and EXAFS signals are sensitive to local structure. Indeed just as XRD is indicative of long-range order, XANES and EXAFS carry signatures of short range order or disorder.
this gives $Z=3.9274$. Thus V has an average valence of approximately $4^+$. *We expect this strong five-fold coordination to effect the electronic properties*, and this is shown to be the case as we show below.

The main input file for FEFF8.2 is generated by Atoms and analysis is done with Athena [5] [version 0.8.037].

Typical XANES spectra for the three different temperatures 90 K, 300 K and 530 K are given, respectively in Figs. 1-3. These are labelled by $\mu_u$ for the unpolarized, by $\mu_{ab}$ for the polarized case representing the ab-plane and by $\mu_c$, when the E vector is parallel to the c-axis.

In Fig. 4 the XANES spectrum is compared with the corresponding projected density of states. The agreement is quite good, showing the correctness of our calculations.

In Fig. 5 the XANES spectra for the two cases, I and II are given using the 90 K input data. Intuitively, one expects that if the axial oxygen position is changed, one would see the consequence of this change in the local electronic structure, i.e. the XANES spectra. In the example given in Fig. 5 we took the apical oxygen fractional $z$-coordinate as $\delta z_{V-OA} = 0.1612$ and labelled this as case I. For comparison we note that the corresponding values of axial oxygen are $\delta z_{V-OA} = 0.1138$ at room temperature for PbTiO$_3$ and $\delta z_{V-OA} = 0.2087$ and $\delta z_{V-OA} = 0.2102$, respectively at 90 K and 300 K for PbVO$_3$, Table I. Thus, for illustration we took an intermediate value between that of PbTiO$_3$ and PbVO$_3$ for this quantity, to see how it would effect the electronic structure. Incidentally, one would also expect roughly this value for the fractional $z$-coordinate for the system PbV$_{0.5}$Ti$_{0.5}$O$_3$, which has not been fabricated yet. It would be useful to fabricate PbV$_{0.5}$Ti$_{0.5}$O$_3$, since it could provide further insight between distortion and multi-ferroic behaviour in these and related systems.

We also expect that varying the tetragonality [c/a] at a given temperature will also effect the XANES spectrum. Indeed this turns out to be the case. This case is labelled as case II. Once again, for demonstration we took an intermediate between that of PbTiO$_3$ [a=b=3.905 Å, c=4.156 Å, c/a=1.06428 at 300 K] and PbVO$_3$ [a=b=3.8033 Å, c=4.4700 Å, c/a=1.1447 at 90 K]. For case II we chose a=b=3.905 Å, c=4.4700 Å, c/a=1.1447 at 90 K.

The positional information [in energy units eV] of the features or peaks for Figs. 1-3 and 5 are given in Table VI.

In order to quantify the change in XANES spectra, as a result of the temperature change, varying the axial oxygen position and the tetragonality at a given temperature, we calculate the difference spectra of the cases with respect to the spectra at 90 K.

The results for difference spectra for the temperatures 300 K and 500 K data with respect to 90 K data are shown in Fig. 6. The difference spectra which result when the axial oxygen position and tetragonality is varied are illustrated in Fig. 7.

Let us consider first some general remarks as a guide to the reader on Vanadium K-edge [7] in the context of Vanadium oxides, in order to motivate the spectra shown in Figs. 1-5. It is known that V forms a series of oxides VO, $V_2O_3$, $V_4O_7$, $V_2O_4$ and $V_2O_5$ over a range of formal oxidation states. In V K-edge XANES/ELNES in these oxides, one observes
a pre-edge absorption feature which is strongest in $V_2O_5$, followed by weak feature/shoulder on a rising absorption edge, which culminates in a strong peak approximately 20 eV from the Fermi energy. It is known that the strong peak is assigned to dipole-allowed transition 1s $\rightarrow$ 4p, the weak shoulder/feature as a shakedown transition representing the 1s $\rightarrow$ 4p and the pre-edge or near-edge feature near the threshold as a forbidden 1s $\rightarrow$ 3d. The features/peaks arising at higher energies than the main 1s $\rightarrow$ 4p transition are more difficult to be specific about. These features may arise from transition to higher np states, multiple scattering and/or shape resonances.

From Figs. 1-3 and 5 we can clearly see five features or peaks. The first peak P1 can be referred to as the edge peak, since it just above the Fermi energy. This feature is present in all the cases. However, there are some interesting points to note, regarding this peak. First of all, the dependence of this peak on the distortion of the local structure around V atom, is evident from our calculation of the different cases. It does not disappear with temperature, since the distortion is present at higher temperatures, in contrast to what would happen in case of centrosymmetric structures. The position of P1 also remains close to approximately 5469.1 eV, Table VI, for all the cases considered here, with the exception of case II, where it is slightly differently located at roughly 5469.4 eV. In order to show and quantify that the distortion and ultimately multi-ferrocity is caused by the asymmetric positions of the axial oxygens, we calculated the polarized XANES data along the c-axis and ab-plane. It is clear from Figs. 1-3 that the main contribution to distortion comes from the c-axis spectra. Thus the unpolarized data $\mu_u$, which is an average of all the polarizations, receives most of the contribution for P1 from the c-axis. In contrast the ab-plane spectra exhibits P1 to a much lesser degree. These points are cleared further by examining P1 in the 530 K spectra, here P1 is quite weak [WF] for the ab-plane data, which effects the polarization average data, so that after averaging P1 appears as a weak [W] feature in the unpolarized spectra, in contrast P1 remains a strong feature in the c-axis spectra.

The strong dependence of the XANES/ELNES on the local distortion is clear not just from P1, but the entire spectrum. For example, P4 [the dominant post edge peak at roughly 5487 eV, is nearly absent for the most non-centrosymmetric case, i.e. the c-axis spectra, Table VI and Figs. 1 3], where we have labelled it as very weak feature [VWF]. P4 would be very large for centrosymmetric case. In short, it anti-correlates with distortion, in contrast to P1 which correlates with deviation from centrosymmetry. On the basis of our data, we can also conclude that P5 also correlates with distortion. The ”shakedown” peaks P2 and P3 are quite robust and only P2 slightly weakens at 530 K, Table VI.

Yet another interesting result of our calculation is that P1 arises, due to the hybridization between the p and d orbitals of the absorber, an effect which is forbidden for centrosymmetric structure but increased by local distortions. This effect is known for PbTiO$_3$ [3], but for PbVO$_3$ it seems to be very pronounced. This is expected due the much bigger tetragonality of the PbVO$_3$ compared to PbTiO$_3$. But our calculations explicitly demonstrate it and further quantifies it in terms of the electronic near edge structure.

The results for the two cases I and II, are displayed in Fig. 5 the five peaks/features
are apparent again. The exact positions of the features are listed in Table VI. It is interesting to note that for case I the peak P4 is dominant compared to P1, whereas it is reversed in case II, Fig. 5. Thus once again we see the anti-correlation of the two peaks P1 and P4, as discussed above. Once again the "shakedown" peaks P2 and P3 are present.

In order to further quantify the near edge electronic structure we have taken the difference spectra, of all the unpolarized cases discussed here, relative to the 90 K spectra. The results are displayed in Figs. 6-7. The percentage change in tetragonality in going from 90 K to 300 K and 530 K, Table I, is approximately 0.6% and 0.9% respectively, with respect to the former. This translates into approximately 4% for the 300 K case and about 10.5% for the 530 K, as can be seen from the difference spectra, Fig. 6, by considering the maximum peak to peak variation. This clearly shows that we can correlate small changes in tetragonality to the local electronic behaviour. Let us turn to Fig. 7 where for case II, the tetragonality was chosen as c/a=1.1447, which is 6.4 % smaller than that of PbVO$_3$ relative to the latter, at the same temperature of 90 K. The change in the corresponding difference spectra is large, as expected, average variation being on the order of 20%. This shows that by taking tetragonality roughly between that of PbTiO$_3$ and that of PbVO$_3$, we can account for the large difference between their electric polarizations, which is incidentally also on the order of 20 %, albeit at different temperature of 300 K. For case I, where we attempted to simulate a behaviour between PbTiO$_3$ and PbVO$_3$, by taking the z-coordinate of the axial oxygen roughly between these two systems, keeping the tetragonality at the same value as PbVO$_3$, we see an average percentage change of 30 % relative to the PbVO$_3$ at the same temperature. In particular variation is large in region of peak P1, as expected in lieu of earlier comments, since the more the deviation from perfect octahedral symmetry, the bigger the effect, clearly the PbVO$_3$ at 90 K has $\delta z_{V-O_A} = 0.2087$ to be compared with $\delta z_{V-O_A} = 0.1612$ for case I, at the same temperature. This represents a percentage change of roughly 23 % in the $\delta z_{V-O_A}$ value relative to the measured PbVO$_3$ at 90 K. In order to see how this effects the difference spectra, we can examine the P1 region in Fig. 7 for case I. Incidentally the change is around 23 %, which is consistent with percentage change of $\delta z_{V-O_A}$.

The charge transfer and occupational orbital numbers are given in Tables VII and VIII. These results can be used to analyze the varying influence of the oxygen environment on the electronic structure of different transition-metal atoms in general, and in particular in the perovskite structure of our interest. Here we only concentrate on a comparison between PbVO$_3$ and PbTiO$_3$, leaving a more detailed comparison between several related materials for future work. The case of PbTiO$_3$ has been calculated in some detail for the purposes of comparison, since it possesses the largest tetragonality among the previous known members of this family. We see that the charge transfer for the oxygen atom in the PbVO$_3$ changes by approximately by 28.9% relative to the PbTiO$_3$ case at 300 K. For the Pb atom one see a change of roughly 16.3 % compared to that in the PbTiO$_3$ system. We note that for each case, the net charge transfer cancels to within ±0.001, which provides a useful and a simple test for our calculations.
The exact location of all the peaks is displayed in Table IX. Both the positive and negative features are presented for obvious reasons. We can immediately see that difference spectra shows the largest variations, and peaks roughly at the positions P1, P2, P3, P4 and P5, discussed above. This is not surprising, but clarifies the differential behaviour of each peak region for the unpolarized spectra given in Figs. 1, 2 and 3.

4 Conclusions

We have for the first time given the XANES study of the newly fabricated PbVO$_3$.

- The spectra for three important cases and the difference spectra have been calculated and presented here. It is demonstrated that electronic structure shows a calculable change in the temperature range 90 - 530 K. This is expected since the c-lattice parameter increases almost linearly with temperature, whereas the a and b lattice constants remain unchanged.

- Roughly speaking all the spectra show five peaks or features in the XANES region.

- We found that by taking polarization into account, we can clearly see the origin and the dependence of peaks and features and their sensitivities, on ab-plane or c-axis. This also allows us to trace back the origin of peaks/features in the unpolarized spectra to the ab-plane and/or c-axis.

- Charge transfers and electronic orbital occupation numbers have been calculated for several cases of interest. We have also given a comparison of charge transfer and orbital occupation numbers between PbVO$_3$ and PbTiO$_3$. For example, we find a change of approximately 28.9% in the charge transfer of the oxygen atom in going from the PbVO$_3$ to the PbTiO$_3$ with respected to the latter, for the 300 K data.

- The difference spectra confirms the previous observations and results, and further correlates the percentage changes in tetragonality and $\delta z_{V-O_A}$ directly to the variations observed in the difference spectra. We can also account roughly for the change in electric polarization between PbVO$_3$ and PbTiO$_3$, by looking at how changes in tetragonality and axial-oxygen deviation from ideal position correlate to the variation in the near edge electronic structure. The difference spectra allows us approximately to translate these into percentage changes.

From these calculation and analysis we can conclude that is possible to quantify the electronic structure of PbVO$_3$ by using the near edge structure.
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Table I: Crystallographic Data at 90 K, 300 K and 530 K for PbVO₃.

| Temperature | Atom | a Å     | c Å     | z/a   | x   | y   | z   |
|-------------|------|---------|---------|-------|-----|-----|-----|
| 90 K        | Pb   | 3.80329(6) | 4.64989(10) | 1.2226 | 0   | 0   | 0   |
|             | V    | 0.5677(3)  | 0.2087(15)  | 0.6919(9) | 1/2 | 1/2 | 0   |
|             | O1   | 0.5677(3)  | 0.2087(15)  | 0.6919(9) | 1/2 | 1/2 | 0   |
|             | O2   | 0.5677(3)  | 0.2087(15)  | 0.6919(9) | 1/2 | 1/2 | 0   |
| 300 K       | Pb   | 3.80391(5) | 4.67680(8)  | 1.2295 | 0   | 0   | 0   |
|             | V    | 0.5668(4)  | 0.2102(15)  | 0.6889(10) | 1/2 | 1/2 | 0   |
|             | O1   | 0.5668(4)  | 0.2102(15)  | 0.6889(10) | 1/2 | 1/2 | 0   |
|             | O2   | 0.5668(4)  | 0.2102(15)  | 0.6889(10) | 1/2 | 1/2 | 0   |
| 530 K       | Pb   | 3.80721(5) | 4.69819(9)  | 1.2340 | 0   | 0   | 0   |
|             | V    | 0.5674(4)  | 0.2102(15)  | 0.6915(10) | 1/2 | 1/2 | 0   |
|             | O1   | 0.5674(4)  | 0.2102(15)  | 0.6915(10) | 1/2 | 1/2 | 0   |
|             | O2   | 0.5674(4)  | 0.2102(15)  | 0.6915(10) | 1/2 | 1/2 | 0   |

Table II: Shell and atom enumeration in the P4mm, with V as a core atom at 90 K.

| Shell | Atom | No.of Atoms | distance from V |
|-------|------|-------------|-----------------|
| 1     | O1   | 1           | 1.66931         |
| 2     | O2   | 4           | 1.98741         |
| 3     | O1   | 1           | 2.98058         |
| 4     | Pb   | 4,4         | 3.35757,3.76839 |
| 5     | V    | 4           | 3.80329         |
| 6     | O1   | 4           | 4.15351         |
| 7     | O2   | 8,4         | 4.29125,4.49449 |
| 8     | V    | 2           | 4.64989         |
| 9     | O1   | 4           | 4.83207         |
| 10    | V    | 4           | 5.37866         |
| 11    | O2   | 4           | 5.56256         |
| 12    | O1   | 4           | 5.63175         |
| 13    | O2   | 4,8         | 5.73409,5.88774 |
| 14    | V    | 8           | 6.00720         |
| 15    | O1   | 4,1         | 6.14930,6.31920 |
| 16    | Pb   | 8,8         | 6.34060,6.56740 |
| 17    | O2   | 8,8         | 6.73848,6.88075 |
Table III: Shell and atom enumeration in the P4mm, with V as a core atom at 300 K.

| Shell | Atom | No.of Atoms | distance from V |
|-------|------|-------------|----------------|
| 1     | O1   | 1           | 1.66775        |
| 2     | O2   | 4           | 1.98583        |
| 3     | O1   | 1           | 3.00905        |
| 4     | Pb   | 4,4         | 3.36742,3.77647|
| 5     | V    | 4           | 3.80391        |
| 6     | O1   | 4           | 4.15345        |
| 7     | O2   | 8,4         | 4.29107,4.52490|
| 8     | V    | 2           | 4.67680        |
| 9     | O1   | 4           | 4.85017        |
| 10    | V    | 4           | 5.37954        |
| 11    | O2   | 4           | 5.58187        |
| 12    | O1   | 4           | 5.63213        |
| 13    | O2   | 4,8         | 5.73437,5.91138|
| 14    | V    | 8           | 6.02845        |
| 15    | O1   | 4,1         | 6.16391,6.34455|
| 16    | Pb   | 8,8         | 6.34658,6.57276|
| 17    | O2   | 8,8         | 6.75478,6.88133|
Table IV: Shell and atom enumeration in the P4mm, with V as a core atom at 530 K.

| Shell | Atom | No.of Atoms | distance from V |
|-------|------|-------------|-----------------|
| 1     | O1   | 1           | 1.67819         |
| 2     | O2   | 4           | 1.99089         |
| 3     | O1   | 1           | 3.02000         |
| 4     | Pb   | 4,4         | 3.37316,3.78862 |
| 5     | V    | 4           | 3.80721         |
| 6     | O1   | 4           | 4.16067         |
| 7     | O2   | 8,4         | 4.29633,4.53410 |
| 8     | V    | 2           | 4.69819         |
| 9     | O1   | 4           | 4.85955         |
| 10    | V    | 4           | 5.38421         |
| 11    | O2   | 4           | 5.61384         |
| 12    | O1   | 4           | 5.63968         |
| 13    | O2   | 4,8         | 5.74051,5.92055 |
| 14    | V    | 8           | 6.04713         |
| 15    | O1   | 4           | 6.17334         |
| 16    | Pb   | 8           | 6.35358         |
| 17    | O1   | 1           | 6.37638         |
| 18    | Pb   | 8           | 6.58357         |
| 19    | O2   | 8,8         | 6.78307,6.88827 |

Table V: Typical oxygen distances in PbVO$_3$ versus PbTiO$_3$ at 300 K, from Pb and M [V,Ti] atoms. The oxygen distances for the two cases I and II at 90 K considered here are also given, in addition to the cases of PbVO$_3$ for 90 K and 530 K. All distances are in Å units.

| Material | Pb-OA  | Pb-OP  | M-OA[short] Å | M-OP Å  | M-OA[long] Å | Z     |
|----------|--------|--------|---------------|---------|--------------|-------|
| PbVO$_3$ | 2.86378| 2.38614| 1.66775       | 1.98583 | 3.00905      | 3.9274|
| PbTiO$_3$| 2.80146| 2.51937| 1.76713       | 1.97916 | 2.38887      | 4.0015|
| Case I   | 2.79184| 2.38090| 1.89018       | 1.98741 | 2.75972      | 3.9099|
| Case II  | 2.91458| 2.38934| 1.60473       | 2.02989 | 2.86527      | 3.4379|
| PbVO$_3$ [90 K] | 2.85907| 2.38090| 1.66931       | 1.98741 | 2.98059      | 3.9099|
| PbVO$_3$ [530 K] | 2.86752| 2.39258| 1.67820       | 1.99089 | 3.0200       | 3.8712|
Table VI: Features/Peaks for Figs. 1-3 and Fig. 5. All the positions are given in eV.

| Case         | P1        | P2        | P3        | P4        | P5        |
|--------------|-----------|-----------|-----------|-----------|-----------|
| 90 K, $\mu_u$ | 5469.087  | 5475.655  | 5480.532  | 5487.475  | 5493.943  |
| 90 K, $\mu_{ab}$ | 5469.087  | 5475.655  | 5480.532  | 5487.475  | VWF       |
| 90 K, $\mu_c$ | 5469.087  | 5475.655  | 5480.532  | VWF       | 5493.943  |
| 300 K, $\mu_u$ | 5469.084  | 5475.652  | 5480.529  | 5487.472  | VWF       |
| 300 K, $\mu_{ab}$ | 5469.084  | 5475.652  | 5480.529  | 5487.472  | VWF       |
| 300 K, $\mu_c$ | 5469.084  | 5476.757  | 5480.529  | VWF       | 5493.943  |
| 530 K, $\mu_u$ | 5469.076  | VW(5476.749) | 5481.216  | 5488.010  | VWF       |
| 530 K, $\mu_{ab}$ | 5469.076  | W(5476.442) | 5481.216  | 5487.464  | VWF       |
| 530 K, $\mu_c$ | 5469.076  | 5476.749  | 5480.521  | VWF       | 5492.951  |
| case I       | 5469.035  | 5479.146  | 5481.175  | 5487.424  | 5496.948  |
| case II      | 5469.387  | 5475.131  | 5479.855  | 5486.627  | 5495.962  |

Table VII: Charge Transfer and Occupation orbital numbers for the polycrystalline PbVO$_3$ at 90 K, 300 K and 530 K. For comparison the case of polycrystalline PbTiO$_3$ at 300 K is given.

| Atom Type        | l character | 90 K    | 300 K   | 530 K   | PbTiO$_3$ [300 K] |
|------------------|-------------|---------|---------|---------|-------------------|
| O                | s           | 1.879   | 1.879   | 1.881   | 1.882, 1.888     |
|                  | p           | 4.357   | 4.355   | 4.361   | 4.448, 4.423     |
|                  | d           | 0.000   | 0.000   | 0.000   | 0.000, 0.000     |
| Charge Transfer  |             | -0.236  | -0.234  | -0.241  | -0.329, -0.312   |
| Atoms in cluster |             | 57      | 57      | 57      | 53, 15           |
| V, Ti            | s           | 0.452   | 0.451   | 0.453   | 0.429, 0.439     |
|                  | p           | 6.653   | 6.653   | 6.655   | 6.663, 6.706     |
|                  | d           | 3.798   | 3.795   | 3.787   | 2.643, 3.792     |
| Charge Transfer  |             | 0.099   | 0.098   | 0.106   | 0.264, 0.081     |
| Atoms in cluster |             | 49      | 45      | 45      | 37, 15           |
| V$_{\text{core}}$, Ti$_{\text{core}}$ | s       | 0.454   | 0.454   | 0.455   | 0.435, 0.439     |
|                  | p           | 6.674   | 6.673   | 6.675   | 6.690, 6.706     |
|                  | d           | 4.902   | 4.922   | 4.894   | 3.778, 3.792     |
| Charge Transfer  |             | -0.037  | -0.037  | -0.031  | 0.095, 0.081     |
| Atoms in cluster |             | 65      | 65      | 57      | 45, 15           |
| Pb               | s           | 1.756   | 1.765   | 1.763   | 1.835, 1.834     |
|                  | p           | 1.300   | 1.298   | 1.285   | 1.141, 1.136     |
|                  | d           | 10.334  | 10.333  | 10.322  | 10.301, 10.331   |
| Charge Transfer  |             | +0.610  | +0.605  | 0.617   | 0.723, 0.699     |
| Atoms in cluster |             | 46      | 46      | 46      | 42, 21           |
Table VIII: Charge Transfer and Occupation orbital numbers for the polycrystalline PbVO$_3$ at for case I and II. For comparison the case of polycrystalline PbTiO$_3$ at 300 K is given.

| Atom Type       | l character | case I at 90 K | case II at 90 K | PbTiO$_3$ [300 K] |
|-----------------|-------------|---------------|----------------|-------------------|
| O               | s           | 1.894         | 1.870          | 1.882, 1.888      |
|                 | p           | 4.442         | 4.315          | 4.448, 4.423      |
|                 | d           | 0.000         | 0.000          | 0.000, 0.000      |
| Charge Transfer |             | -0.335        | -0.185         | -0.329, -0.312    |
| Atoms in cluster|             | 57            | 57             | 53, 15            |
| O               | s           | 0.451         | 0.439          | 0.429, 0.439      |
|                 | p           | 6.685         | 6.638          | 6.663, 6.706      |
|                 | d           | 3.612         | 3.869          | 2.643, 3.792      |
| Charge Transfer |             | 0.249         | 0.052          | 0.264, 0.081      |
| Atoms in cluster|             | 49            | 45             | 37, 15            |
| V, Ti           | s           | 0.452         | 0.443          | 0.435, 0.439      |
|                 | p           | 6.693         | 6.662          | 6.690, 6.706      |
|                 | d           | 4.779         | 4.971          | 3.778, 3.792      |
| Charge Transfer |             | 0.088         | -0.069         | 0.095, 0.081      |
| Atoms in cluster|             | 65            | 65             | 45, 15            |
| Pb              | s           | 1.767         | 1.752          | 1.835, 1.834      |
|                 | p           | 1.145         | 1.408          | 1.141, 1.136      |
|                 | d           | 10.334        | 10.339         | 10.301, 10.331    |
| Charge Transfer |             | +0.756        | +0.502         | 0.723, 0.699      |
| Atoms in cluster|             | 46            | 43             | 42, 21            |
Table IX: Peak positions in eV, of the difference spectra displayed in Figs. 6-7.

| Peak Type | $\delta\mu_{90-300}$ | $\delta\mu_{90-530}$ | $\delta\mu_{90-case1}$ | $\delta\mu_{90-case2}$ |
|-----------|----------------------|----------------------|------------------------|------------------------|
| +ve       | 5468.787             | 5469.087             |                        |                        |
| +ve       | 5469.687             |                      |                        |                        |
| +ve       | 5470.626             |                      |                        |                        |
| +ve       | 5475.131             | 5475.131             |                        |                        |
| +ve       | 5477.341             | 5477.341             | 5477.341               |                        |
| +ve       | 5480.532             |                      |                        |                        |
| +ve       | 5481.227             |                      | 5481.227               |                        |
| +ve       |                      | 5484.989             |                        |                        |
| +ve       | 5486.627             |                      |                        |                        |
| +ve       | 5488.342             |                      |                        |                        |
| +ve       |                      | 5492.962             |                        |                        |
| -ve       | 5468.687             | 5468.187             |                        |                        |
| -ve       |                      | 5469.387             | 5469.687               |                        |
| -ve       | 5474.626             |                      | 5474.626               |                        |
| -ve       |                      | 5476.198             |                        |                        |
| -ve       |                      | 5478.56              |                        | 5479.198               |
| -ve       | 5480.532             |                      |                        |                        |
| -ve       | 5481.941             | 5481.941             |                        |                        |
| -ve       |                      | 5484.199             |                        |                        |
| -ve       | 5488.342             |                      |                        |                        |
| -ve       | 5491.057             |                      |                        |                        |
| -ve       | 5492                 |                      |                        | 5497                   |
Figure 1: XANES $\mu$ data generated with FEFF8.2 for the $p4mm$ phase of PbVO$_3$ at the V K-edge. Shown are the unpolarized, polarized with $E||ab$ and $E||c$ data, when the temperature is 90 K.

Figure 2: Same as Fig. 1 for the 300 K case.

Figure 3: Same as Fig. 1 for the 530 K case.

Figure 4: XANES $\mu$ 90 K data generated with FEFF8.2 for the $p4mm$ phase of PbVO$_3$ at the V K-edge, and compared to the corresponding projected density of states.

Figure 5: XANES $\mu$ data generated with FEFF8.2 for the $p4mm$ phase of PbVO$_3$ at the V K-edge at 90 K for the two cases I and II.

Figure 6: Difference $\mu [\mu_{90} - \mu_i, i=300,530]$ spectra of temperatures 300 K and 530 K with respect to the spectra at temperature 90 K.

Figure 7: Difference $\mu [\mu_{90} - \mu_{casei}, i=I,II]$ spectra for the two cases I and II at 90 K with respect to the spectra at temperature 90 K.