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## Anharmonicity and disorder in simple and complex perovskites: a high energy synchrotron and hot neutron diffraction study

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**Abstract.** We report a study of simple ABO<sub>3</sub> type perovskites BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, KNbO<sub>3</sub>, SrTiO<sub>3</sub> and the relaxor perovskites PbSc<sub>1/2</sub>Nb<sub>1/2</sub>O<sub>3</sub> (PSN) in their cubic phase using hard synchrotron radiation and hot neutrons. Gram–Charlier expansions of the thermal parameters have been performed and have revealed interesting features about the probability density function and the one-particle potential of the different atoms. This description is compared with other descriptions in terms of the split atom model and in terms of the rotator model. Structural trends regarding the order–disorder versus displacive character of the phase transitions have been obtained. It is concluded that SrTiO<sub>3</sub> and BaTiO<sub>3</sub> are quasi-harmonic systems whereas KNbO<sub>3</sub> shows weak anharmonicity and PbTiO<sub>3</sub> and PSN display strong anharmonic features.

### 1. Introduction

During recent years phase transitions have been traditionally divided into order–disorder and displacive. In the displacive case the potential energy of the system is supposed to vary with temperature, being (quasi)harmonic at high temperature and displaying multiple wells *below*  $T_c$ , the system standing in one of the minima at an off-centre position. When the temperature rises, the distance between the two minima should diminish until  $T_c$  where the gap between the wells should disappear. In contrast, in the order–disorder situation the potential energy of an atom versus its displacement should be temperature independent and remain multi-welled at all temperatures. In this case it is the orientation of the local distortions which changes with temperature, showing a collective orientation below  $T_c$ .

Later it was pointed out that the local distortions in the displacive case should not be zero just above  $T_c$  because of critical fluctuations and that, in the order–disorder case, the magnitude of the local distortions should never be constant because of elastic deformations. This points out similarities between both mechanisms which are physically distinct: in the displacive case an instability resulting from long range cooperative interactions produces the local distortion whereas in the order–disorder case the local distortions are due to local instabilities.

Nowadays, it is admitted that most real systems are in between order–disorder and displacive cases which are in fact two theoretical ideal cases, one where the ratio  $J/\Delta V$  ( $J$  being the coupling constant which drives the transition and  $\Delta V$  the order–disorder gap) is zero (order–disorder limit), the other one where this ratio is infinite (displacive limit). This approach appeared to be efficient from experimental and theoretical points of view. Recently Pérez-Mato *et al* have been able within the  $\phi^4$  model to relate this  $J/\Delta V$  ratio to empirical parameters such as the Curie constants at  $T_c^+$  and  $T_c^-$ , the Rhodes–Wohlfarth parameter etc [1–3].

Phase transitions in simple perovskites were among the first examples to be extensively studied, in particular ferroelectric systems such as BaTiO<sub>3</sub>, KNbO<sub>3</sub> and PbTiO<sub>3</sub> and ferroelastic systems such as SrTiO<sub>3</sub>. The order–disorder versus displacive debate in these systems started when Comes *et al* observed x-ray diffuse intensity for BaTiO<sub>3</sub> and KNbO<sub>3</sub> in the form of sets of planes normal to the cubic axes [4]. This anomalous intensity was attributed to one-dimensional long range correlations of *static* displacements of the Ti or Nb ions in the cubic phase, conferring an order–disorder character to the different phase transitions. In this model the crystal potential energy for the cubic perovskite should display eight degenerate minima along the  $\langle 111 \rangle$  directions, corresponding to displacements of the Ti or Nb ion (eight-site model). This point seemed to receive confirmation by the structural study of BaTiO<sub>3</sub> by Itoh *et al* [5]. However, afterwards Hüller was able to explain the diffuse pattern of BaTiO<sub>3</sub> by a quasi-harmonic model [6], which received confirmation from inelastic-scattering studies in which soft-optic dipoles interactions were observed, whereas Comes' model implies a relaxational dynamic of hoppings among the different sites. An x-ray study by Tanaka *et al* came afterwards in support of this Hüller mechanism [7]. On the other hand, several reports supported the order–disorder picture, for instance EXAFS and XANES measurements [8, 9].

Later this discussion was extended to the cubic phase of PbTiO<sub>3</sub> by Nelmes *et al* [10] who used both anharmonic and split atom refinements of their diffraction data, which support an order–disorder character for the phase transition. This latter observation was surprising since lead titanate had so far been considered to be a 'textbook' displacive system, in particular from inelastic neutron diffusion experiments.

The case of SrTiO<sub>3</sub> is even less conclusive. Hutton and Nelmes, using neutron scattering [11], and Maslen *et al*, using synchrotron radiation [12], showed the absence of any anharmonicity in the probability density function of all atoms, even close to  $T_c$ ; on the other hand Abramov *et al* obtained with conventional x-ray experiments a disordered model of SrTiO<sub>3</sub> at room temperature and at 145 K [13].

Many studies of ABO<sub>3</sub> perovskites (for instance Raman-scattering experiments) have suggested, in particular for BaTiO<sub>3</sub>, a complicated coupling of the soft-mode picture with order–disorder hoppings. In fact, the extent of order–disorder versus displacive character and the types of motion taking place at the transitions remain unsettled: this is largely due to the strongly damped character of the order parameter as well as the different characteristic time scales which are probed by the different techniques. It is now recognized that many phase transitions exhibit a two-time-scale response in which very slow fluctuations manifest themselves in a central peak in the dynamical response.

In parallel to this experimental situation, many improvements in the understanding of these systems have been made using first principles calculations on ferroelectric ABO<sub>3</sub> perovskites (e.g. [14]), since the pioneering works by Cohen [15]. For instance LAPW calculations have been able to investigate the complex perovskite PZT ground state and piezoelectric properties of simple and complex perovskites [16]. The interest of complex perovskites comes from a special class of ferroelectric materials known as 'relaxor ferroelectrics', which possess a high dielectric constant changing very smoothly with temperature and displaying a strong

frequency dispersion. Most of these materials are lead-based perovskite compounds with general  $\text{PbBB}'\text{O}_3$  formula. Several microscopic explanations have been proposed for their unusual dielectric properties but these explanations are difficult to ascertain due to a lack of structural information. However, all the proposed models require, at a certain level, some kind of disorder or inhomogeneity, and from this standpoint the experimental situation is very complex.

Of course exact structural models, which include local displacements, are strongly needed to perform interatomic potential calculations. Indeed, even though the average distortion from the high-symmetry structure is represented by the order parameter, the actual local distortion can be quite different. This disorder should be included in first principles calculations in order to obtain the exact ground state of these systems.

We have recently reported a comparative structural study of simple ( $\text{PbTiO}_3$  and  $\text{BaTiO}_3$ ) and complex perovskites ( $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ , PSN, which is a relaxor and  $\text{BaSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  BSN) using conventional x-ray and neutron sources [17]. In this study we have tested the possibility of disordered shifts in the cubic phase: compounds with Ba show no evidence of disorder whereas compounds with Pb reveal possible (static or dynamic) shifts of the lead atoms.

In this paper we present a diffraction study of the cubic phases of  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{KNbO}_3$ ,  $\text{SrTiO}_3$  and relaxor  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  perovskites using high energy (short wavelength) synchrotron radiation at ESRF and at the hot neutron source at ILL. A comparison of these results with previous ones is presented.

## 2. Data analysis

In a quasi-harmonic system the local structure differs from the average structure due to lattice vibrations but in disordered systems the difference is more substantial. It is then useful and usual since pioneering works by Zucker and Schulz, Kuhs, Boysen etc [18–20] to introduce the probability density function PDF( $\mathbf{u}$ ) which measures the probability of finding at a temperature  $T$  a certain atom at a position  $\mathbf{u}$ . In a perfectly ordered crystal with quasi-harmonic dynamical state the PDF will have a single Gaussian shape

$$\text{PDF}_0(\mathbf{u}) = (2\pi \langle u^2 \rangle)^{-3/2} \exp(-u^2/2\langle u^2 \rangle)$$

where  $\langle u^2 \rangle$  is the mean square displacement.

This PDF provides direct information on the effective potential  $V(\mathbf{u})$  of the atoms involved: for any given atoms this function is an average over the positions of all other atoms through the relation

$$\text{PDF}(\mathbf{u}) = \exp^{-V(\mathbf{u})/kT} / Z = \text{PDF}(0) \exp^{-V(\mathbf{u})/kT}$$

where  $Z$  is the partition function of the Boltzmann statistics.

A peak of the PDF occurs at a minimum of  $V$ ; the PDF can therefore tell whether the potential function has the form of a single or multiple well, thus providing an important clue about the mechanism driving a phase transition.

In a diffraction experiment the PDF is probed through the refinement of the temperature factor from the structure factor expansion

$$F(\mathbf{Q}) = \sum_j f_j(\mathbf{Q}) T_j(\mathbf{Q})$$

where  $f_j$  is the atomic diffraction factor of the  $j$ th atom,  $\mathbf{Q}$  the diffraction vector and  $T_j(\mathbf{Q})$  is the temperature factor equal to  $\exp[(-1/2)\langle (\mathbf{Q} \cdot \mathbf{u})^2 \rangle]$ .

The relation between the temperature factor and the PDF is

$$T_j(\mathbf{Q}) = \int \text{PDF}(\mathbf{u}) \exp(i\mathbf{Q} \cdot \mathbf{u}) d^3\mathbf{u}.$$

In the framework of the harmonic approximation,  $T_j(\mathbf{Q})$  reduces to  $T_{j0}(\mathbf{Q})$  and one recovers the harmonic PDF<sub>0</sub> through  $u_{iso}$  isotropic or  $u_{ij}$  anisotropic Debye–Waller factors which are classically extracted from diffraction data. Assuming a cubic cell with lattice parameter  $a$  and  $h, k, l$  the Miller index gives

$$T_{j0}(\mathbf{h}) = \exp(-2\pi^2/a^2(u_{11}h^2 + u_{22}k^2 + u_{33}l^2 + u_{12}hk + \dots)).$$

Several developments of the temperature factor have been proposed in order to take into account the anharmonicity; they are intensively discussed in the work of Kuhs (e.g. [19]). Gram–Charlier expansion is nowadays commonly used. The starting point is the differential expansion of a harmonic (Gaussian) PDF<sub>0</sub>.

$$\text{PDF}(\mathbf{u})_{anh} = \text{PDF}_0(1 - C^j D_j + (1/2!)C^{jk} D_j D_k - (1/3!)C^{jkl} D_j D_k D_l + (1/4!)C^{jklm} D_j D_k D_l D_m - \dots)$$

where  $D_j$  is the differential operator  $\delta/\delta u^j$  and  $C^{jkl\dots}$  the tensorial coefficients known as quasi-moments. Using the relation with the  $N$ -dimensional Hermite polynomials  $H_{ijk\dots n}$ :

$$(-D)^N \text{PDF}_0(\mathbf{u}) = H_{ijk\dots n}(\mathbf{u}) \text{PDF}_0(\mathbf{u}) = (-1)^N (\delta^N / \delta^i \delta^j \delta^k \dots \delta^n)$$

allows a numerical evaluation of the generalized PDF<sub>anh</sub>. The standardized Gram–Charlier expansion is obtained by omitting first and second order terms to reduce correlation. One obtains for the generalized temperature factor

$$T_j(\mathbf{Q}) = T_{j0}(\mathbf{Q})[1 + (i^3/3!)(C^{jkl} Q_j Q_k Q_l) + (i^4/4!)(D^{jklm} Q_j Q_k Q_l Q_m) + (i^5/5!) \times (E^{jklmn} Q_j Q_k Q_l Q_m Q_n) + (i^6/6!)(F^{jklmno} Q_j Q_k Q_l Q_m Q_n Q_o) + \dots] \quad (1)$$

where  $C^{jkl}$ ,  $D^{jklm}$ ,  $E^{jklmn}$ ,  $F^{jklmno}$ , ... are the anharmonic tensors of third, fourth, fifth, ... order.

In the case of a simple ABO<sub>3</sub> cubic perovskite with  $Pm\bar{3}m$  symmetry the average structure is quite simple since all atoms sit on special Wyckoff positions. Thus, one has easily the possibility of extracting information on deviations from the average structure through refinements of  $T_j(\mathbf{Q})$  temperature factors. Moreover, due to the centrosymmetry of the sites, all odd anharmonic tensors  $C^{jkl}$ ,  $E^{jklmn}$  etc are zero. At the fourth order development, we obtain for A and B cations only one  $u_{11} = u_{iso}$  harmonic component and two fourth order components  $D^{1111}$  and  $D^{1122}$ , and for the oxygen atoms two harmonic  $u_{11}$  and  $u_{33}$  and three fourth order  $D^{1111}$ ,  $D^{2222}$  and  $D^{1122}$  components. Thus in addition to the standard harmonic situation where three coefficients have to be refined, we obtain only five more high order coefficients. If high- $Q$  ( $\sin \Theta/\lambda$ ) data are obtained one can relatively easily obtain a reliable PDF for each atom. Moreover, due to the simplicity of the structure such refinements can be easily performed from powder diffraction data; Boysen for instance [20] has extensively performed Rietveld anharmonic analysis of different compounds. In the case of  $Pm\bar{3}m$  the symmetry is so high that the intensities can be extracted directly from powder pattern without any profile (Rietveld) refinement because all the powder overlaps of  $h, k, l$  (like 333 and 511) are not model dependent; therefore the extraction is straightforward and these intensities can be directly used in single crystal refinement programs.

In this study we have used a combination of x-ray powder diffraction on the BM 16 diffractometer at ESRF with  $\lambda = 0.34987 \text{ \AA}$  and the neutron four-circle diffractometer D9 with  $\lambda = 0.541 \text{ \AA}$  at ILL. For one compound (SrTiO<sub>3</sub>) supplementary data at ESRF on the ID11 diffractometer ( $\lambda = 0.21379 \text{ \AA}$ ) and at LLB on the 6T2 diffractometer ( $\lambda = 0.904 \text{ \AA}$ ) were collected. In all cases the short wavelengths used have allowed us to collect the large set of data necessary to perform reliable anharmonic refinements, as well as to suppress or minimize extinction/absorption effects which are classically observed to be drastic in the structural studies of these perovskites.

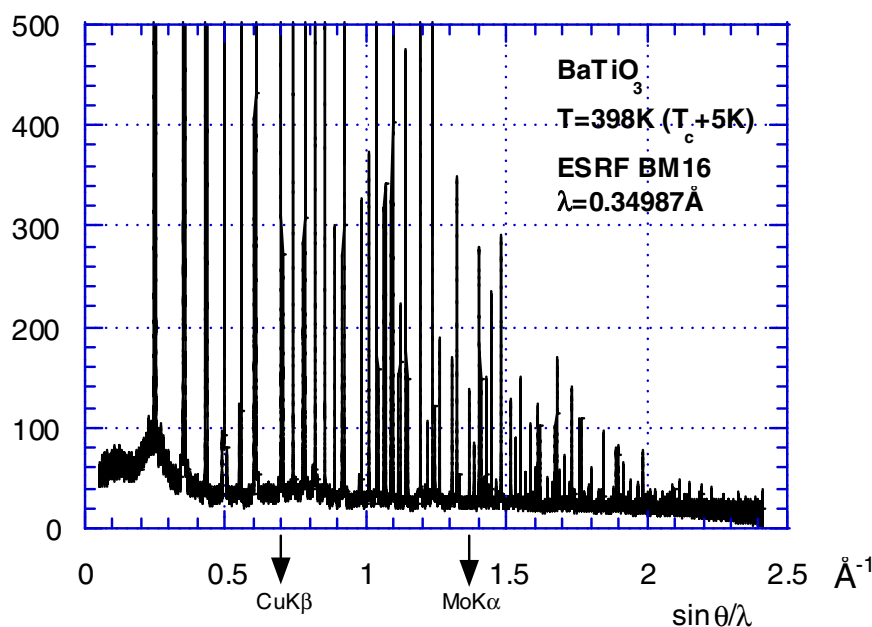


Figure 1. Powder diffraction pattern of BaTiO<sub>3</sub> recorded on BM16 diffractometer at ESRF.

Single crystals of BaTiO<sub>3</sub> ( $4 \times 3 \times 4 \text{ mm}^3$ ), KNbO<sub>3</sub> ( $3 \times 4 \times 2 \text{ mm}^3$ ) and SrTiO<sub>3</sub> (a polished sphere of  $40 \mu\text{m}$  radius) were grown according to the usual methods. These samples were thoroughly checked for the existence of twins. Powder samples of PbTiO<sub>3</sub> and PSN were synthesized starting from stoichiometric amounts of the corresponding oxides as in [17]. The synthesized samples were well crystallized and no presence of parasitic phases was evidenced by x-ray diffraction and chemical analysis. The powder samples of BaTiO<sub>3</sub> and SrTiO<sub>3</sub> consisted of commercial batches from Johnson and Matthey with purity  $>99.99\%$ . The samples were ground to obtain a uniform grain size ( $5 \mu\text{m}$ ) and annealed to avoid all residual constraints.

Figure 1 shows a typical synchrotron x-ray powder diffraction pattern obtained for BaTiO<sub>3</sub> in the cubic phase at  $T = T_c + 5 \text{ K} = 398 \text{ K}$ . We have indicated the classical cut-off (copper K $\beta$  and molybdenum K $\alpha$ ) obtained with conventional sources: with the very short wavelength we used, a very large set of supplementary data is obtained. Intensities were extracted from powder patterns and anharmonic refinements were performed using Jana98/Jana2000 packages. D9 neutron data were collected using a PSD allowing a three-dimensional integration of the intensities, corrected for TDS (which was revealed to be in fact negligible) and Becker–Coppens type I extinction. BM16 and ID11 data revealed no significant extinction/absorption effect.

### 3. Results

We have summarized in table 1 the experimental conditions and numerical results for the different compounds.

#### 3.1. SrTiO<sub>3</sub> and BaTiO<sub>3</sub>

In both compounds no anharmonicity was evidenced at any temperature.

**Table 1.** Results of the different anharmonic refinements. For PbTiO<sub>3</sub> and PSN, rotator refinements with radius  $r$  are also included (see the text).

	BaTiO <sub>3</sub>	KNbO <sub>3</sub>	SrTiO <sub>3</sub>			PbTiO <sub>3</sub>		PbSc <sub>1/2</sub> Nb <sub>1/2</sub> O <sub>3</sub>	
Sample type	Crystal	Crystal	Crystal			Powder		Powder	
Technique	Neutron	Neutron	X-ray			X-ray		X-ray	
Diffractometer	D9	D9	ID11			BM16		BM16	
Wavelength (Å)	0.5415	0.5415	0.2137			0.349 87		0.349 87	
Temperature (K)	400 ( $T_c + 7$ )	715 ( $T_c + 7$ )	300 ( $T_c + 195$ )	130 ( $T_c + 25$ )	873 ( $T_c + 110$ )	773 ( $T_c + 10$ )		523 ( $T_c + 160$ )	
Total/indep. number of peaks	1293/152	1112/170	2680/328	2615/289	64/64	72/72		83/83	
Cell param. (Å)	4.0079	4.0100	3.905	3.903	3.9731	3.9670		4.0780	
$R_w$ (%)	1.28	1.27	0.89	1.00	1.36	0.98	1.04	1.68	1.71
A cation ( $u$ Å <sup>2</sup> )	0.0054(1)	0.0156(1)	0.0068(1)	0.0031(1)	0.0415(2)	0.0314(3)	$r = 0.26(1)$ Å	0.0462(4)	$r = 0.32(1)$ Å
$D^{1111}$ (10 <sup>4</sup> )						-0.0264(36)	$u = 0.0111(11)$	-0.109(6)	$u = 0.0125(9)$
$D^{1122}$ (10 <sup>4</sup> )						-0.0157(15)		-0.024(3)	
B cation ( $u$ Å <sup>2</sup> )	0.0084(1)	0.0119(1)	0.0047(1)	0.0027(1)	0.0198(6)	0.0129(4)		0.0051(4)	
$D^{1111}$ (10 <sup>4</sup> )		-0.0046(3)							
$D^{1122}$ (10 <sup>4</sup> )		-0.0007(1)							
O $u_{11}$ (Å <sup>2</sup> )	0.0082(1)	0.0161(1)	0.0105(1)	0.0063(1)	0.0397(22)	0.0294(4)		0.0312(28)	
$u_{33}$ (Å <sup>2</sup> )	0.0075(1)	0.0085(1)	0.0038(1)	0.0033(1)	0.0285(33)	0.0153(20)		0.0178(10)	

For SrTiO<sub>3</sub> we have compared results obtained from data collected at ESRF, on the BM16 powder diffractometer at room temperature and on the ID11 single crystal CCD diffractometer at room temperature and at  $T_c + 15$  K, as well at LLB on the 6T2 neutron four-circle diffractometer at room temperature. At room temperature ( $T_c + 195$  K) the harmonic  $u_{ij}$  parameters obtained by all these different techniques were the same within the esd. Therefore in table 1 we only give the ID11 results. The values of  $u$  for Sr and Ti diminish when cooling to 130 K ( $T_c + 25$  K) from 0.0068(1) Å<sup>2</sup> to 0.0031(1) Å<sup>2</sup> and from 0.0047(1) Å<sup>2</sup> to 0.0027(1) Å<sup>2</sup> and the  $u_{11}$  and  $u_{33}$  of oxygen change from 0.001 05(1) Å<sup>2</sup> and 0.0038(1) Å<sup>2</sup> to 0.0063(1) Å<sup>2</sup> and 0.0033(1) Å<sup>2</sup>. These values are to be compared with Hutton values obtained at  $T_c + 5$  K: 0.002 48(7) Å<sup>2</sup> for Sr, 0.0021(1) Å<sup>2</sup> for Ti and 0.005 57(6) Å<sup>2</sup> and 0.0022(1) Å<sup>2</sup> for O [11]: the agreement is fair. The strong anisotropy of  $u_{ij}$  for oxygen is maintained to low temperatures. This anisotropy is classically observed in perovskites and was reported for first time by Hewat in his pioneering study of ferroelectric perovskites: it was explained by the existence of a low frequency mode of rotation of oxygen octahedra [21].

Attempt to refine the anharmonic fourth order for strontium, titanium or oxygen (separately and together) gives no gain in  $R$  factors as well as complete correlation between  $u_{ij}$  and  $D^{ijklm}$ .

In the case of BaTiO<sub>3</sub>, we have used the data obtained from the D9 neutron four-circle diffractometer at temperature 400 K ( $T_c + 7$  K). The conventional refinement gives a (harmonic) thermal parameter in very good agreement from our previous results obtained from neutron powder diffraction ( $\lambda = 1.2226$  Å with  $\sin \Theta / \lambda_{max} = 0.77$  Å<sup>-1</sup> in [17] from which we transformed  $\beta_{ij}$  into  $u_{ij}$ ): indeed we obtain for Ba  $u_{iso} = 0.0054(1)$  Å<sup>2</sup> instead of 0.0063(8) Å<sup>2</sup>, for Ti 0.0084(1) Å<sup>2</sup> instead of 0.068(15) Å<sup>2</sup> and for O  $u_{11} = 0.0082(1)$  Å<sup>2</sup> and  $u_{33} = 0.0075(1)$  Å<sup>2</sup> instead of 0.0084(2) Å<sup>2</sup> and 0.0080(4) Å<sup>2</sup>. We can notice that the allowed anisotropic values for oxygen gives in fact quasi-isotropic values. Attempts to refine the anharmonic fourth order for barium, titanium or oxygen (separately and together) give no significant improvement. Data obtained from synchrotron powder diffraction at BM16 (figure 1) confirmed also the absence of anharmonicity at  $T_c + 7$  K and  $T_c + 100$  K (the results are not shown).

From this we conclude that strontium and barium titanate display harmonic behaviour, even in the close vicinity of the para-ferro phase transition.

### 3.2. KNbO<sub>3</sub>

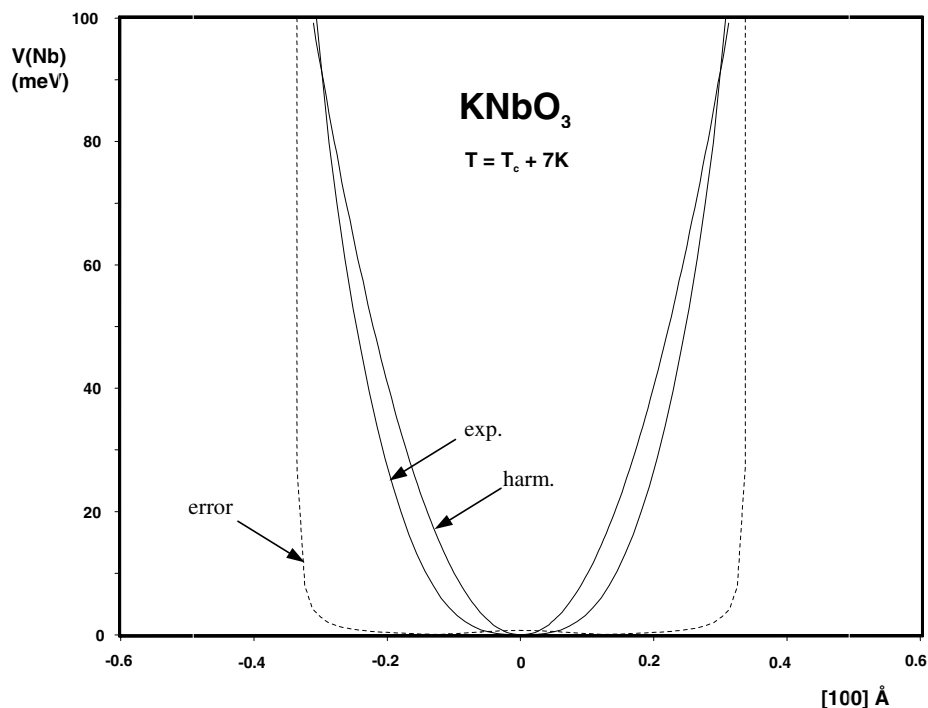
In KNbO<sub>3</sub> the situation is slightly different as small but significant deviations from harmonic behaviour can be detected.

Experimental conditions were the same as in BaTiO<sub>3</sub> (see table 1), i.e. single crystal neutron diffraction on D9; the temperature of the experiment was just above the critical temperature, at 715 K ( $T_c + 7$  K). Harmonic refinements converged in few cycles to the values of  $u$ : 0.0156(1) Å<sup>2</sup> for K, 0.0132(1) Å<sup>2</sup> for Nb and 0.0164(1) Å<sup>2</sup> ( $u_{11}$ ) and 0.0089(1) Å<sup>2</sup> ( $u_{33}$ ) for oxygen. No data exist (to our knowledge) for this compound in the cubic phase, but regarding potassium, Hutton and Nelmes [11] obtained in KMnF<sub>3</sub> at  $T_c + 10$  K a value of 0.0132(1) Å<sup>2</sup>. The value for niobium is standard and a strong anisotropy for oxygen is observed. When fourth order coefficients are refined for niobium, the  $R$  factor changes from 1.75% to 1.67% with no deviation for  $u$  except a slight diminution for niobium from 0.0132 Å<sup>2</sup> to 0.0119(1) Å<sup>2</sup>; attempts to develop to sixth order give no gain and total correlation between  $D^{ijklm}$  and  $F^{jklmno}$ . Attempts to refine anharmonic fourth order coefficients for the other atoms gives no significant results.

The one-particle potential is drawn in figure 2 for niobium along the (100) direction and is compared to parabolic behaviour: the experimental potential is observed to be smoother than



the harmonic case along the six  $\langle 100 \rangle$  cubic directions.



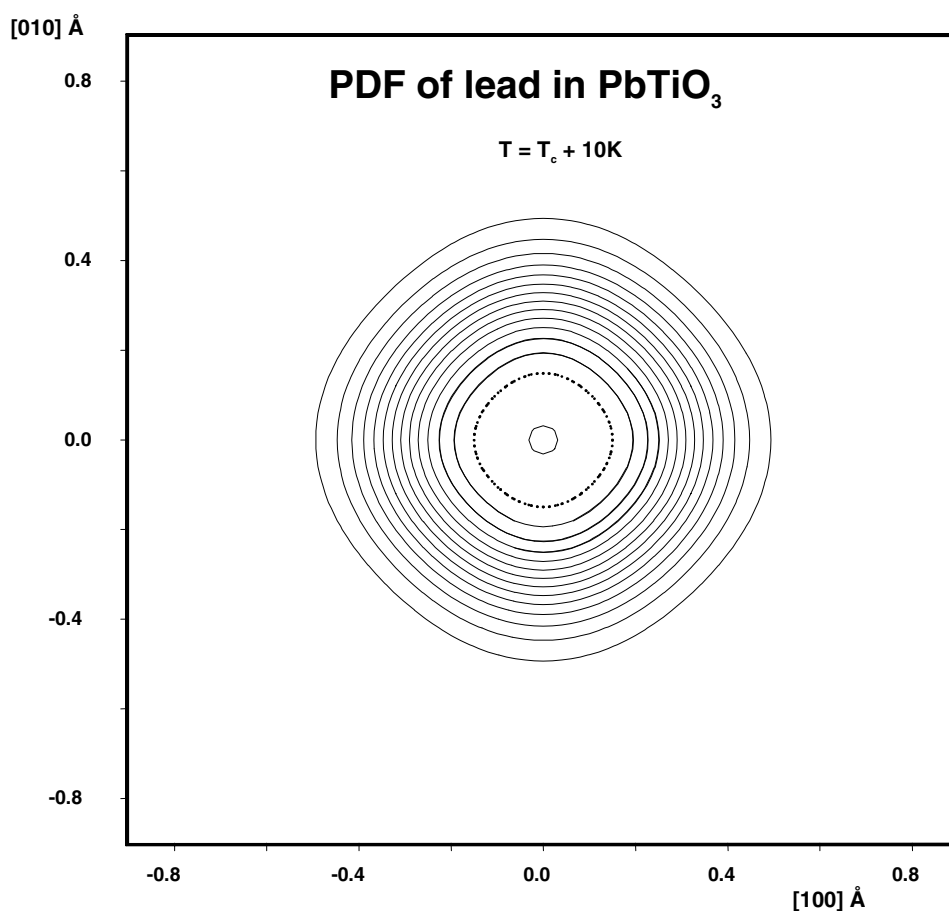
**Figure 2.** Harmonic, experimental (anharmonic) and error curve of potential  $V(u)$  for an Nb atom in  $\text{KNbO}_3$ , along the  $[100]$  cubic direction.

### 3.3. $\text{PbTiO}_3$

In this compound strong deviations from the harmonic behaviour have already been reported from single crystal data collections at ILL on D9 by Nelmes *et al* [10]. They have shown an order–disorder character of the phase transition close to  $T_c$  because the PDF of the lead atom could be described as split atoms over the six different  $\langle 100 \rangle$  directions. We have performed a synchrotron powder data collection on BM16 at two temperatures: one at 873 K, far above  $T_c$  ( $T_c + 110$  K), one at 773 K, just above  $T_c$  ( $T_c + 10$  K).

At 873 K no deviation from harmonic behaviour could be evidenced;  $u$  for lead is  $0.0415(2) \text{ \AA}^2$  in perfect agreement with our (unpublished) previous measurement ( $0.0420 \text{ \AA}^2$ ) (conventional x-ray powder diffraction at  $\lambda = 1.39223 \text{ \AA}$  with  $\sin \Theta / \lambda_{max} = 0.69 \text{ \AA}^{-1}$ ); these results are different from the value measured in [10] (recalculated from their  $u_t = 3u_{iso}$ , between  $0.027 \text{ \AA}^2$  and  $0.037 \text{ \AA}^2$ , depending on the structural model), but the comparison is difficult to make because these  $u$  values were obtained in anharmonic and split atom refinements. The  $u$  value for titanium is  $0.0198(6) \text{ \AA}^2$  (instead of  $0.0110 \text{ \AA}^2$  for our previous measurement, and  $0.0151 \text{ \AA}^2$  from [10]). The oxygen atoms revealed some anisotropy:  $u_{11} = 0.0397(22) \text{ \AA}^2$  and  $u_{33} = 0.0285(33) \text{ \AA}^2$  ( $0.0288$  and  $0.0127 \text{ \AA}^2$  from [10]).

At 773 K  $u$  for lead, titanium and oxygen changed to respectively  $0.0314(3) \text{ \AA}^2$ ,  $0.0129(4) \text{ \AA}^2$  and  $u_{11} = 0.0294(4) \text{ \AA}^2$  and  $u_{33} = 0.0153(20) \text{ \AA}^2$ . These values are in fair agreement for lead and titanium and higher for oxygen if we compare with our previous value at

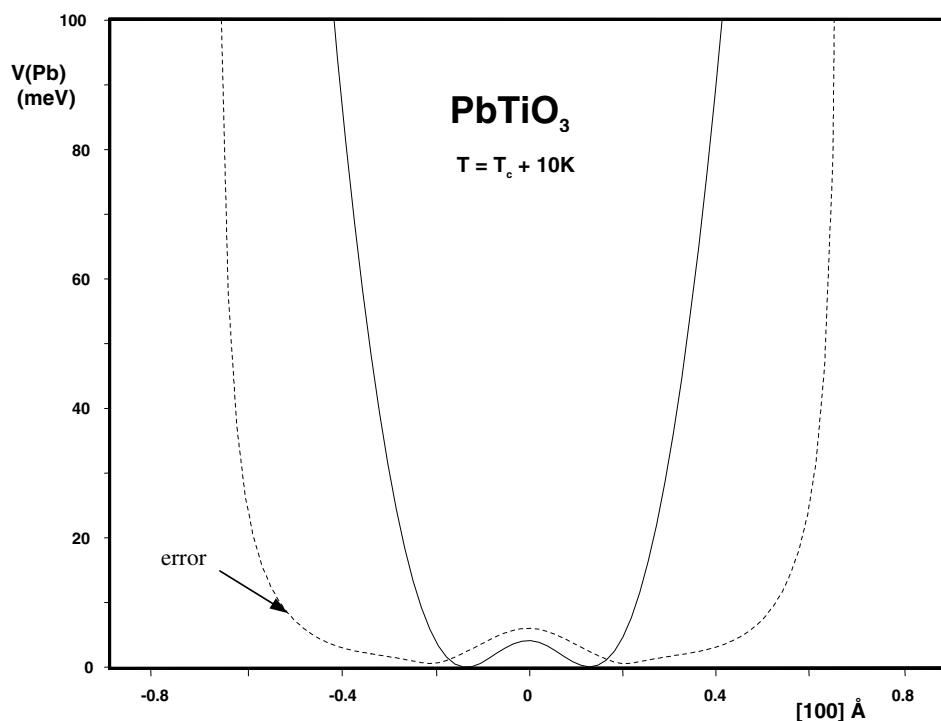


**Figure 3.** PDF of lead atom in the (110) plane for  $\text{PbTiO}_3$ . The dotted curve is the maximum probability for lead.

765 K, 0.0385(7), 0.0180(5), 0.010(3), 0.007(3)  $\text{\AA}^2$  (lead, titanium and oxygen respectively), obtained from neutron powder diffraction ( $\lambda = 1.2226 \text{ \AA}$  with  $\sin \Theta / \lambda_{max} = 0.77 \text{ \AA}^{-1}$ , [17]).

At this temperature strong anharmonicity could be evidenced for lead atoms: introducing the two fourth order  $D^{ijklm}$  has allowed us to reduce strongly the agreement  $R$  factor from 1.41% (harmonic case) to 0.98%. The PDF in the (110) plane and the one-particle potential along the [100] direction are shown in figures 3 and 4. The PDF is no longer spherical but elongated along the  $\langle 100 \rangle$  sixfold directions. The potential is very flat: in fact the absolute minimum is no longer at the origin in 000 position but stands at  $r_0 = \pm 0.15 \text{ \AA}$ , the minima being separated by a weak gap of  $\approx 5 \text{ MeV}$ ; however this gap is within the e.s.d. (see the error curve from figure 4).

Split atom solutions for lead have also been tested along different cubic directions ([100], [110], [111] and general [123] directions); these tests reveal classical 100% correlations between the value of the shift position and  $u_{iso}$ . We have overcome this difficulty by imposing a fixed shifted position value  $\delta$ , refining only  $u_{iso}$  and measuring the  $R$  factor, as we did in [17]: an  $R$  versus  $\delta$  curve is constructed for the different directions. For all the direction we obtain a minimum at  $R \approx 1.25\%$  and  $\delta \approx 0.20 \text{ \AA}$  with an associated  $u \approx 0.017 \text{ \AA}^2$ .



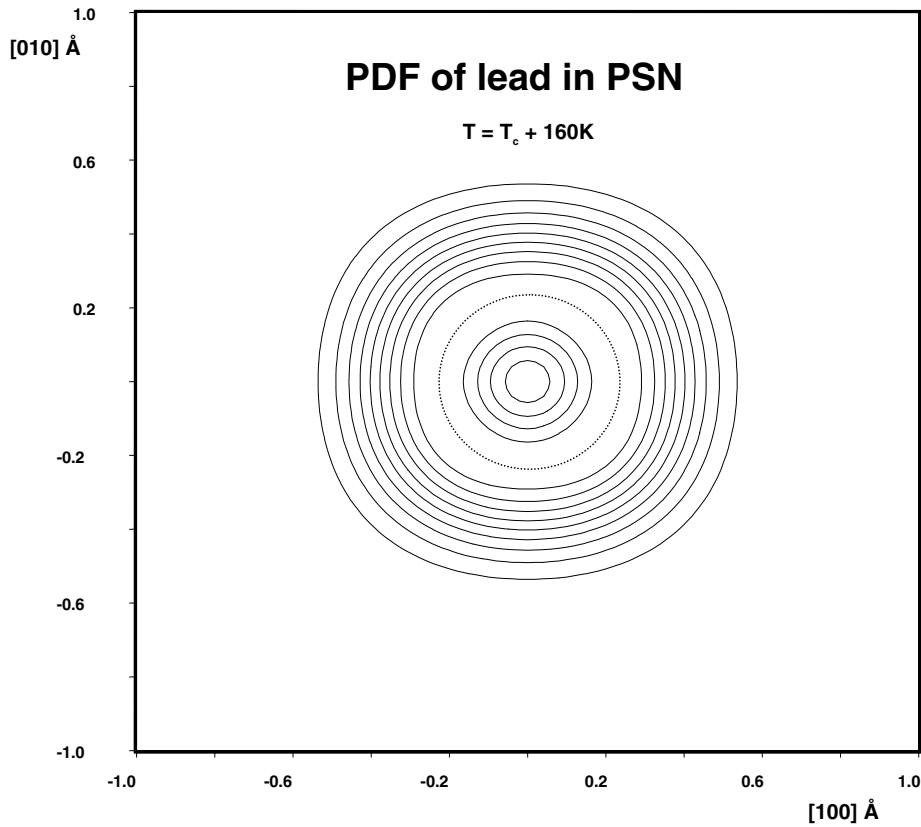
**Figure 4.** Experimental (anharmonic) and error curve of potential  $V(u)$  for a Pb atom in  $\text{PbTiO}_3$ , along the [100] cubic direction, corresponding to the PDF of figure 3. The observed gap is within the e.s.d. (error curve).

Using the same data we have also tested a ‘rotator’ solution for lead positions: that is the atom is allowed to sit on a sphere of radius  $r$ . We have obtained a slightly less good agreement ( $R = 1.04\%$ ) with  $r = 0.26 \text{ \AA}$  and  $u = 0.0111(11) \text{ \AA}^2$ . Other attempts at high order development for titanium or oxygen atoms, as well as sixth order for lead, give no gain and total correlation between  $D^{jklm}$  and  $F^{jklmno}$ .

### 3.4. $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$

In the case of relaxor compounds of the  $\text{PbBB}'\text{O}_3$  type the B site of the  $\text{ABO}_3$  perovskite is randomly occupied by two cations B and B'; moreover in the cubic phase of these compounds, disordered (random) shifts of lead have already been suspected from conventional x-ray split atom refinements. Indeed experiments performed in  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  [22] revealed disordered shift along simple cubic directions. However further experiments in  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  [17], in  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  and  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  [23] seemed to indicate *isotropic* disordered shifts. In particular Zhukov *et al* showed that the non-isotropic shifts arise from low  $\sin \Theta / \lambda$  cut-off and disappear when higher  $Q$  data are used [23].

We have performed a synchrotron powder experiment on the BM16 diffractometer at 523 K ( $T_c + 160 \text{ K}$ ), which shows very strong deviations from harmonic behaviour. In the harmonic refinement  $u$  values for Pb and Sc/Nb are respectively  $0.0521(4) \text{ \AA}^2$  and  $0.0080(4) \text{ \AA}^2$  and  $u_{11}$  and  $u_{33}$  for oxygen atoms are  $0.0312(28) \text{ \AA}^2$  and  $0.0178(10) \text{ \AA}^2$ . These values are in fair agreement except for oxygen with our previous neutron powder data ( $\lambda = 1.2226 \text{ \AA}$



**Figure 5.** PDF of a lead atom in the (110) plane for PSN. The dotted curve is the maximum probability for lead.

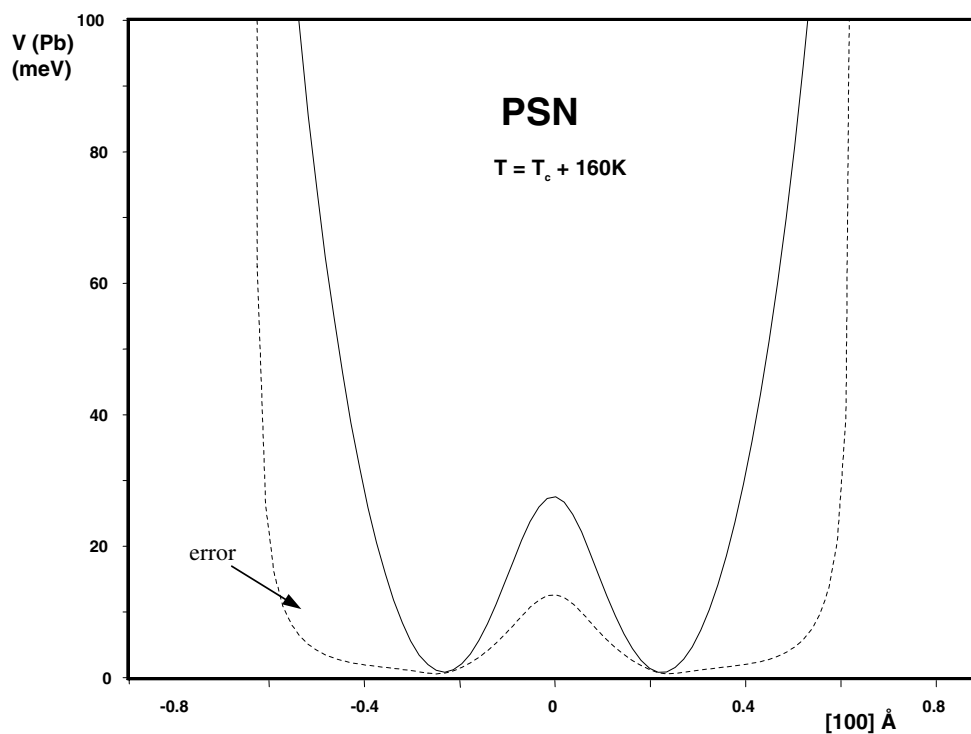
with  $\sin \Theta / \lambda_{max} = 0.77 \text{ \AA}^{-1}$ ) where we obtain respectively for Pb, Sc/Nb and O atoms  $u_{iso} = 0.0548 \text{ \AA}^2$  and  $0.0106 \text{ \AA}^2$ , and  $u_{11} = 0.011(3) \text{ \AA}^2$  and  $u_{33} = 0.006(3) \text{ \AA}^2$  [17].

Allowing the refinement of the two independent  $D^{jklm}$  coefficients for lead gives a strong reduction of the  $R$  factor from 2.38% to 1.68% and  $u$  of lead reduces to  $0.0462(4) \text{ \AA}^2$ . The PDF is no longer spherical but now spherical-shell shaped, and therefore the cut through the (110) plane reveals minima along a circle (figure 5). But unlike  $\text{PbTiO}_3$  at 873 K, the potential along the [100] direction (figure 6) displays a strong gap (out of the e.s.d.),  $\Delta V \approx 30 \text{ meV}$ , to be compared with  $kT = 50 \text{ meV}$ , separating the two minima at  $r_0 = \pm 0.23 \text{ \AA}$ .

As we did in the last paragraph for  $\text{PbTiO}_3$ , split atom solutions for lead have also been tested along different cubic directions ([100], [110], [111] and general [123] directions): for all the directions we obtain a minimum at  $R \approx 1.98\%$  and  $\delta \approx 0.25 \text{ \AA}$  with an associated  $u \approx 0.018 \text{ \AA}^2$ .

We have also tested a 'rotator' solution for lead positions as we did for  $\text{PbTiO}_3$ . We have obtained an almost equivalent agreement ( $R = 1.71\%$ ) with  $r = 0.32 \text{ \AA}$  and  $u = 0.0125 \text{ \AA}^2$ .

Other attempts at fourth order development for titanium or oxygen atoms, as well as sixth order for lead, give no significant gain and total correlation between  $D^{jklm}$  and  $F^{jklmno}$ .



**Figure 6.** Experimental (anharmonic) and error curve of potential  $V(u)$  for a Pb atom in PSN, along the [100] cubic direction, corresponding to the PDF of figure 4. The observed gap is of the order of  $kT$  and clearly out of the e.s.d., as revealed by the error curve: lead atoms have maximum probability of sitting in a spherical shell of radius 0.25 Å.

#### 4. Discussion and conclusion

Using hard synchrotron radiation and hot neutrons have allowed us to perform Gram–Charlier expansions of the thermal parameters for simple  $ABO_3$  type perovskites  $BaTiO_3$ ,  $PbTiO_3$ ,  $KNbO_3$ ,  $SrTiO_3$  and the relaxor perovskites  $PbSc_{1/2}Nb_{1/2}O_3$  (PSN) in their cubic phase. Our results show grossly three different behaviours:  $SrTiO_3$  and  $BaTiO_3$  behave as a harmonic system,  $KNbO_3$  displays some weak anharmonicity and lead perovskites reveals strong anharmonic features.

Regarding  $SrTiO_3$ , as we mentioned in the introduction there are some contradictory results in the literature for this compound. Indeed a report by Abramov *et al* using conventional x-rays [13] revealed intriguing results. These authors reported at room temperature and at 145 K ( $T_c + 40$  K) a PDF for titanium where the atom is randomly spherically shifted from its special position and a PDF for oxygen with two randomly occupied positions along [100] shifted at  $\pm 0.06$  Å; for Sr they observed at  $T_c + 40$  K strong anharmonicity which appears when the temperature is changed from 300 to 145 K. Our results clearly are in agreement with those by Hutton and Nelmes [11] and Maslen *et al* [12] and confirm the absence of these effects, which are probably due to correlations via scale factor between thermal parameters and extinction/absorption effects, usually very strong for such compounds in the case of conventional x-ray diffraction on single crystals.

For  $BaTiO_3$  and  $KNbO_3$ , as shortly reviewed, the contribution of the order–disorder versus

displacive regime is still a matter of debate. Our results for BaTiO<sub>3</sub> show no deviation and for KNbO<sub>3</sub> small deviations from harmonicity. In the case of BaTiO<sub>3</sub> Itoh *et al* reported a disordered structure just above  $T_c$  [5]. Indeed, introducing disordered shifts of the Ba and Ti atoms from their special positions of the cubic phase of BaTiO<sub>3</sub> allowed an improvement of structure refinements. However the gain obtained on the  $R$  agreement factor was extremely small (some  $10^{-3}$  on the  $R$  factor, i.e. 1.506% instead of 1.512% for shifts of the Ti atoms) and may result again from correlations between different parameters of refinements. In fact our results support Hüller's model [6] which explained the diffuse scattering observed by Comes *et al* [4] by a quasi-harmonic model in which correlation functions of Ti atoms with a strong directional dependence are introduced [8]. Indeed we have observed a harmonic potential for titanium. On the other hand as the potential which is probed in the Gram–Charlier development is a one-particle potential, i.e. where the atoms are supposed to vibrate independently, we have no information about the existence of correlation of titanium vibrations.

Lead perovskites are peculiarly interesting because they reveal a strong anharmonicity: lead atoms have definitively a different behaviour from strontium, barium and potassium atoms. In this study we have compared three different types of structural model for PbTiO<sub>3</sub> and PSN: split atoms, rotator and anharmonic PDF.

As is well known, there is a mathematical equivalency between an anharmonic model of displacement with infinite terms in equation (1) and a split atom refinements with infinite number of sites. In a real situation where truncations exist, the anharmonic description is usually better at least from the standpoint of convergence and flexibility to adapt to a real situation. However high  $Q$  data are necessary in order to obtain reliable results and if unavoidable, split atom models, as in our previous Rietveld study, are at least a step toward a more precise description than simple harmonic model.

In the present study of lead perovskites we have obtained also a good refinement of the data using a rotator model where the lead is shifted from its special position by a  $|r|$  value. This type of refinement is in our opinion a good alternative to split atom refinements, when more or less isotropic disorder is suspected (like in some hydrogen compounds): it can be seen like a split atom model of a specific (spherical) type but with an infinite (continuous) number of positions. However from a general point of view Gram–Charlier expansion should be preferred as it provides the possibility to adapt *a priori* much more complex (non-spherical) situations.

In our previous study of lead titanate [17] with data obtained from conventional diffraction we have observed anomalously high thermal parameters of lead atoms. A reduction toward normal values, in the vicinity of  $T_c$ , with better agreement factors could be obtained when (isotropic) shifts were imposed, but such an effect disappeared at higher temperatures. The amplitude of the shift (0.20 Å) obtained from this split atom procedure, that we also tested in the present study, is midway between the distance between minima measured from the anharmonic treatment (0.15 Å) and the radius of the rotator solution (0.26 Å). The PDF description gives better fits than the split atom model although the rotator model also gives almost the same agreement factor (respectively 0.98, 1.25 and 1.04%). So we believe that the PDF description is closer to reality than a simple split atom model. Regarding a comparison with the rotator model, on the one hand the one-particle potential extracted from the present anharmonic refinement is flat close to the minimum, but on the other hand we observed a possible very small gap between any  $\pm r_0$  shifted positions (figure 4). That means that in this particular case both descriptions, rotator and anharmonic, which lead to almost equivalent agreement factors are probably, almost physically equivalent and should anyway be preferred to the more simplistic split atom description. The main difference between the anharmonic and rotator models is that the PDF we have obtained for lead indicates an elongation along  $\langle 100 \rangle$  cubic directions. This result is an example of what one can get from an anharmonic refinement as a

supplementary information, compared to a rotator model obviously isotropic. When heating this effect disappears and a harmonic potential is recovered.

These results are in qualitative agreement with neutron results by Nelmes *et al* [10]; however these authors gave preference to a six-site disordered model. We believe that the present description in terms of an anharmonic one-particle potential study give a more precise description of the lead behaviour in  $\text{PbTiO}_3$  close to  $T_c$  (at higher temperature both studies indicated quasi-harmonic behaviour). We cannot exclude that at temperatures closer to  $T_c$  one may pass to a six-site disorder model, as a prefiguration of the macroscopic shift which occurs below  $T_c$  inside the ferroelectric tetragonal phase. In all cases, the temperature evolution of the PDF from harmonic to anharmonic when approaching  $T_c$  is clearly to be associated with the critical character of the phase transition and it indicates a strong order–disorder component of this phase transition close to  $T_c$ .

The situation is even more complex for the relaxor  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PSN) compound. Here strong deviations from harmonicity were observed far above  $T_c$  ( $T_c + 160$  K). The three-dimensional PDF is in the form of a spherical shell with a radius  $r$  of  $0.23$  Å and the gap between the minima is  $30$  MeV, which is close to  $kT = 50$  MeV. As for  $\text{PbTiO}_3$  a ‘classical’ split atom refinement gives less satisfactory agreement and a ‘rotator’ solution gives an almost equivalent description to the anharmonic one (respectively 1.98, 1.71 and 1.68%). The amplitude of the shift obtained from the split atom procedure ( $0.25$  Å) is also midway between the distance between minima measured from the anharmonic treatment ( $0.23$  Å) and the radius of the rotator solution ( $0.32$  Å).

PSN is a disordered compound where both Sc and Nb cations statistically occupy the B site of the perovskite. This implies that locally two types of octahedron exist. Therefore one may wonder whether a static contribution to the (harmonic and anharmonic) thermal parameters exists. In the case of  $\text{PbTiO}_3$  the observed disorder is obviously critical and therefore dynamic, because it appears only close to  $T_c$ . Moreover it disappears when cooling to the tetragonal phase (below  $T_c$ ), the structure of this phase giving no evidence of disorder [24]. In the case of PSN the situation is more complex. The disorder is observed in the cubic phase far above  $T_c$ , while in the ferroelectric phase the disorder does not disappear completely. Indeed, at  $T_c$ , cooperative shifts of lead are observed along the  $\langle 111 \rangle$  direction, inducing the rhombohedral ferroelectric phase, but some disorder remains, as evidenced by split atom refinements of the ferroelectric phase from neutron and x-ray experiments [17] showing a disordered component of polarization perpendicular to the  $\langle 111 \rangle$  direction. In fact, at  $T_c$  there is a reduction or condensation of a three-dimensional disorder toward a two-dimensional one. We have also observed this situation in the trigonal phase of  $\text{PMN}_{0.9}/\text{PT}_{0.1}$  [25].

The best description for the thermal vibrations of lead atoms in complex relaxor perovskites like PSN is probably a description in term of vibrations inside an isotropic spherical shell potential with a gap of the order of  $kT$ : this implies that the lead atom can easily rotate inside the spherical shell but also jumps between disordered positions at  $\pm r$ . This situation probably gives rise to complex dynamical phenomena with interesting relaxational processes that we are now trying to investigate using time of flight quasi-elastic studies.

In conclusion we hope that our results have shed some light on the intriguing problem of disorder in simple perovskites. The direct measurement of the anharmonic character of potential wells in perovskites near the transition temperature may be useful for splitting the order–disorder and displacive contributions to the phase transition dynamics. The selectivity of diffraction techniques to the crystallographic sites is in principle an advantage for probing the anharmonicity of the different atoms, generally attributed to the non-linear polarizability of their electronic structures.

Our results in relaxor perovskite PSN give a strong experimental support to the recent

model of a relaxor by Blinc *et al* [26], which is a spherical random-bond/random-field model and has as an essential ingredient isotropic or quasi-isotropic disordered spins/dipoles. We have obtained recent results in relaxor PMN which also support this model [27].

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