CARPY, A., AMESTOY, P. & GALY, J. (1972). *C. R. Acad. Sci. Sér. C*, **275**, 833–835.
CARRUTHERS, J. R. & WATKIN, D. L. (1979). *Acta Cryst.* A**35**, 698–699.
CARRUTHERS, J. R. & WATKIN, D. L. (1986). *CRYSTALS*. Issue 9. Chemical Crystallography Laboratory, Oxford, England.
CATTI, M. & FERRARIS, G. (1976). *Acta Cryst.* A**32**, 163–165.
FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
FLACK, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
GASPERIN, M. (1975). *Acta Cryst.* B**31**, 2129–2130.
ISHIZAWA, N., MARUMO, F., IWAI, S. & KIMURA, M. (1977). *Annu. Meet. Mineral. Soc. Jpn*, p. 68.
ISHIZAWA, N., MARUMO, F., KAWAMURA, T. & KIMURA, M. (1975). *Acta Cryst.* B**31**, 1912–1915.
JAMESON, G. B., SCHNEIDER, R., DUBLER, E. & OSWALD, H. R. (1982). *Acta Cryst.* B**38**, 3016–3020.
LICHTENBERG, F., WIDMER, D., BEDNORZ, J. G., WILLIAMS, T. & RELLER, A. (1991). *Z. Phys.* B**82**, 211–216.
MACLEAN, D. A., NG, H.-N. & GREEDAN, J. E. (1979). *J. Solid State Chem.* **30**, 35–44.
MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1020.
Molecular Structure Corporation (1989). *TEXSAN. Single-Crystal Structure Analysis Package*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
MÜLLER, G. (1988). *Acta Cryst.* B**44**, 315–318.
NANAMATSU, S., KIMURA, M., DOI, K., MATSUSHITA, T. & YAMADA, Y. (1974). *Ferroelectrics*, **8**, 511–513.
NANAMATSU, S., KIMURA, M., DOI, K. & TAKAHASHI, M. (1971). *J. Phys. Soc. Jpn*, **30**, 300–301.
NANAMATSU, S., KIMURA, M. & KAWAMURA, T. (1975). *J. Phys. Soc. Jpn*, **38**, 817–824.
NANOT, M., QUEYROUX, F. & GILLES, J. C. (1973). *C. R. Acad. Sci. Sér. C*, **277**, 505–507.
PORTIER, R., FAYARD, M., CARPY, A. & GALY, J. (1974). *Mater. Res. Bull.* **9**, 371–378.
ROLLETT, J. S. (1965). *Computing in Crystallography*, edited by J. S. ROLLETT, p. 40. Oxford: Pergamon.
SANTORO, A. (1974). *Acta Cryst.* A**30**, 224–231.
SCHEUNEMANN, K. & MÜLLER-BUSCHBAUM, H.-K. (1975). *J. Inorg. Nucl. Chem.* **37**, 1879–1881.
SCHNERING, H. G. VON & BLECKMANN, P. (1968). *Naturwissenschaften*, **55**, 342–343.
TANAKA, M., SEKII, H. & OHI, K. (1985). *Jpn. J. Appl. Phys.* **24**(Suppl. 2), 814–816.
WILLIAMS, T., SCHMALLE, H., RELLER, A., LICHTENBERG, F., WIDMER, D. & BEDNORZ, G. (1991). *J. Solid State Chem.* **93**, 534–548.
YAMAMOTO, N., YAGI, K., HONJO, G., KIMURA, M. & KAWAMURA, T. (1980). *J. Phys. Soc. Jpn*, **48**, 185–191.

Acta Cryst. (1993). B**49**, 244–254

Phasons Modulate the Atomic Debye–Waller Factors in Incommensurate Structures: Experimental Evidence in $ThBr_4$ at 55 K*

BY G. MADARIAGA, J. M. PÉREZ-MATO AND I. ARAMBURU

Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 *Bilbao, Spain*

(*Received* 13 *July* 1992; *accepted* 25 *September* 1992)

Abstract

The incommensurate displacive structure of β-$ThBr_4$ at 55 K has been determined from a neutron diffraction data set including main reflections and first-order satellites. The superspace group is $P^{I4_1/amd}_{s\,1\,s1}$. Final agreement factors are 0.0193, 0.0186 and 0.045 for all, main and satellite reflections, respectively. It is shown that the effect of phasons on the atomic Debye–Waller factors can be quantified by two additional structural parameters: the modulus $\beta^{Br}_{11,2}$ and the phase $\chi^{Br}_{11,2}$ of a second harmonic that spatially modulates the temperature factors of Br atoms. Results are in good agreement, within the resolution of the experimental data, with the theoretically expected value for $\chi^{Br}_{11,2}$. Crystal data for the average structure: $M_r = 551.65$, tetragonal, $I4_1/amd$, $a = 8.919\ (1)$, $c = 7.902\ (1)$ Å, $V = 628.6\ (2)$ Å^3, $Z = 4$, $D_x = 5.82$ Mg m^{-3}, $\lambda = 0.84$ Å, wavevector $\mathbf{q} = 0.32\mathbf{c}^*$.

* Preliminary results of this work were presented at the International Workshop on Methods of Structural Analysis of Modulated Structures and Quasicrystals, Lekeitio, Spain, May 1991.

1. Introduction

The experimental detection of phase-fluctuation effects on the temperature factors of incommensurate (IC) structures is still unresolved in structural determination. Indeed, the quantitative evaluation of these effects has been a subject of controversy in some descriptions of IC structures. The theoretical formulation of the influence of these low-frequency excitations on the Debye–Waller factors has followed a path of increasing complexity from the simplest Overhauser (1971) approach to its final recently established general form (Currat & Janssen, 1987; García, Pérez-Mato & Madariaga, 1989; Pérez-Mato & Madariaga, 1990; Pérez-Mato, Madariaga & Elcoro, 1991).

Overhauser's fomulation of the phason Debye–Waller factor (PDWF) introduces a surprising overall factor, $\exp(-\frac{1}{2}n^2\langle\delta\varphi^2\rangle)$, dependent on the mean-

0108-7681/93/020244-11$06.00

squared phase fluctuations $\langle\delta\varphi^2\rangle$ and the order of satellites, n, though independent of the atom type, the Bragg angle and, even, of the static modulation regime. These unusual features are also present in the (commonly accepted) Axe (1980) version of the PDWF, $\exp[-\frac{1}{2}n(n-1)\langle\delta\varphi^2\rangle]$, although in this formulation first-order satellites are unaffected by the PDWF. However, within Axe's approach the possibility of modulated temperature factors also appeared. This fact was also pointed out by Yamamoto (1982) and Paciorek & Kucharczyk (1985), in later work.

Experimental studies based on the temperature dependence of satellite intensities (Chapman & Colella, 1984, 1985; Ehses, 1985; Colella, 1989) as well as on IC structure refinements (Steurer & Adlhart, 1983), tried to elucidate the correctness of the above-mentioned PDWF formulae. In all cases the results were ambiguous or unconvincing. This fact can be easily understood if it is kept in mind that these PDWFs act as additional scale factors for the satellites and hence are highly correlated with other parameters and may absorb experimental systematic errors and/or the structural evolution of the static distortion. In this way it is worth noting that in the first attempt to confirm the Overhauser PDWF formula (Chapman & Colella, 1984; Colella, 1989), the authors insisted on the use of absolute intensities as an essential condition for PDWF detection but they overlooked the temperature dependence of the static structure.

The general form of the Debye–Waller factors (DWFs) in an IC structure has been fomulated within a rigorous context (García, Pérez-Mato & Madariaga, 1989). The resulting expressions imply that atomic DWFs are atomic and modulated, as usually happens with other atomic parameters in IC phases, and they cannot be reduced in general to an overall factor. Indeed, these results corroborate the intuitive expressions of modulated atomic DWFs previously formulated as a consequence of the continuous variation of each atomic site neighbourhood in an IC structure. Therefore the atomic and modulated DWF should be strongly dependent on the structural regime of the static modulation.

As a particular case and with use of the Landau model to describe the basic IC phase transition, the influence of the amplitude and phase modes on the atomic DWF of an IC phase in a sinusoidal regime can be explicitly accounted for. Such modes provoke, on the one hand, the appearance of an important contribution to some (or all) of the normal homogeneous atomic DWFs. On the other hand, the atomic DWFs become spatially modulated by a second harmonic. The moduli and phases of both (zeroth- and second-order) harmonics are completely determined, for each atom, by those of the primary static distortion and the mean square of the amplitude and phase fluctuations.

The first attempt to confirm these predictions experimentally was made with a conventional X-ray data set used for the determination of the IC structure of thiourea (Madariaga *et al.*, 1990). Only a partial agreement with the above predictions was achieved. In the case of thiourea the main problems arise from the weakness of the searched-for effect on the diffraction pattern (probably, a more accurate and careful data collection would be necessary) together with the relatively large number of correlated parameters to refine and the significant anharmonicity of the atomic displacement functions. A sinusoidal IC structure described with a few parameters and suspected to be affected by phase fluctuations seems more adequate for a search of phason effects in DWFs. β-$ThBr_4$ possesses these characteristics. The high site symmetry of Th and Br atoms and the direction of the modulation wavevector simplifies its structural distortion. On the other hand, phase and amplitude branches have been clearly observed by inelastic neutron scattering (Bernard *et al.*, 1983; Currat, Bernard & Delamoye, 1986).

At 95 K, $ThBr_4$ undergoes a phase transition from a tetragonal phase (space group $I4_1/amd$, $Z = 4$) to a one-dimensional displacive IC structure. Below this temperature, neutron diffraction measurements (Bernard *et al.*, 1983; Currat, Bernard & Delamoye, 1986) show the presence of weak first-order satellites, which indicates a structural distortion with wavevector $\mathbf{q} = 0.32\mathbf{c}^*$. No lock-in transition has been detected within the temperature range 95 to 1.5 K. Weak second-order satellites seemed to be observed at very low temperatures (Currat, Bernard & Delamoye, 1986) but they could not be accurately measured. This fact, together with the observed temperature independence of the wavevector (Currat, Bernard & Delamoye, 1986), implies that the static distortion remains almost sinusoidal even at temperatures far below 95 K.

The aim of this work is to present the incommensurately modulated structure of $ThBr_4$ and, as a result, the first experimental evidence of what is expected to occur when the most characteristic IC excitations, phasons and amplitudons, are considered in a structural refinement. Special attention was paid to any source of possible errors that may have masked these subtle contributions.

2. Experimental

Neutron diffraction data of $ThBr_4$ were supplied by J. Pannetier and R. Currat at ILL (Grenoble). The data set consisted of reflections collected at 100 K (basic structure) and at 55 K (IC phase). Raw inten-

Table 1. *Crystal data and some data-collection parameters of* $ThBr_4$ *at* 100 *and* 55 K

Temperature (K)	55	100
λ (Å)	0.84	0.84
Cell parameters (Å)	$a = 8.919$ (1)	$a = 8.921$ (1)
	$c = 7.902$ (1)	$c = 7.912$ (2)
$(\sin\theta/\lambda)_{max}$ (Å^{-1}) ($hkl0$)	0.8394	0.5968
$(\sin\theta/\lambda)_{max}$ (Å^{-1}) ($hkl \pm 1$)	0.416	
Maximum $hkl0$	14,10,13	10,7,9
Measured reflections		
Total	1323	331
Main	991	
Satellite (first-order)	332	
Independent reflections		
Main (observed $I > 3\sigma$)	434 (389)	162
R_{int}	0.021	0.018
Observed satellites	54	
R_{int}	0.039	

sities measured at 100 K as well as those corresponding to main reflections belonging to the IC phase were previously averaged by the authors of the data collection, under the Laue group $4/mmm$. In both cases reflections expected to be systematic absences of the space group $I4_1/amd$ were not measured. The whole set of incommensurate satellites (including symmetry equivalents) collected at 55 K was available as a list of $|F_{obs}|$ and $\sigma(|F_{obs}|)$ calculated from counting statistics. Their intensities ($|F_{obs}|^2$) were averaged under the point group $4/mmm$, showing an excellent internal R factor. Reflections of the structure at 100 K and main reflections of the IC phase were corrected for Lorentz factor but not for absorption. Those 'main' reflections, of both basic and IC structures, with $I < 3\sigma(I)$ and satellites with $|F_{obs}| < 6\sigma(|F_{obs}|)$ were flagged as unobserved. Because of their dubious quality, observed during the averaging, five additional first-order satellites (5301, 6311, 622$\bar{1}$, 213$\bar{1}$ and 4331) were also excluded from the reflection list. Table 1 summarizes relevant information concerning the experimental conditions and the quality of collected data.

3. Refinement of the basic and average structures

The basic structure at 100 K and the average structure (with the use of only the main reflections of the IC data set) at 55 K, have been determined* for a better comparison with previously published results. Both structures are tetragonal and isostructural. Their space group is $I4_1/amd$ with $Z = 4$. In both structures there are only two independent atoms (one Br and one Th) occupying special positions. The site symmetries are $\bar{4}2m$ and m for Th and Br atoms, respectively. Full-matrix least-squares refinements were carried out. During the last cycles of refinement one extra parameter accounting for an empirical extinction correction was included. Because of the strong correlation between the extinction parameter and the elements of the atomic thermal tensors, several programs [*XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), *SHELX*76 (Sheldrick, 1976) and *MSR* (Paciorek & Uszynski, 1987)], and also therefore different extinction-correction formulae, were tried. Final results and agreement factors are listed in Tables 2 and 3, respectively. Notice that the refined parameters agree within the standard deviations and, therefore, should be considered as

Table 2. *Comparative results (see text) for the commensurate structure at* 100 K *and the average structure at* 55 K *of* $ThBr_4$

Thermal parameters, in β form, are multiplied by 10^5. The only extradiagonal element allowed by symmetry, β_{23}^{Br}, having value almost zero, has been omitted for simplicity. Estimated standard deviations are given in parentheses. Extrapolated results are from the data of Currat *et al.* (1986).

	x_0	y_0	z_0	β_{11}	β_{22}	β_{33}
Commensurate structure at 100 K						
Th						
XRAY system	0	$\frac{3}{4}$	$\frac{1}{8}$	52 (5)	52 (5)	57 (9)
*SHELX*76	0	$\frac{3}{4}$	$\frac{1}{8}$	42 (7)	42 (7)	66 (13)
Extrapolated				42	42	117
Br						
XRAY system	0	0.56411 (6)	0.79788 (7)	553 (7)	107 (7)	139 (9)
*SHELX*76	0	0.5641 (1)	0.7979 (1)	541 (7)	92 (7)	151 (13)
Extrapolated				598	84	132
Average structure						
Th						
XRAY system	0	$\frac{3}{4}$	$\frac{1}{8}$	24 (2)	24 (2)	66 (3)
*SHELX*76	0	$\frac{3}{4}$	$\frac{1}{8}$	22 (2)	22 (2)	70 (3)
MSR	0	$\frac{3}{4}$	$\frac{1}{8}$	25 (2)	25 (2)	70 (3)
Extrapolated				10	10	66
Br						
XRAY system	0	0.56425 (3)	0.79771 (4)	665 (5)	69 (2)	114 (3)
*SHELX*76	0	0.5643 (0)	0.7977 (0)	667 (5)	65 (2)	114 (3)
MSR	0	0.56425 (4)	0.79771 (4)	667 (5)	72 (2)	117 (3)
Extrapolated				722	57	66

Table 3. *Agreement factors corresponding to the different refinements of the commensurate at* 100 K *and the average structure at* 55 K *of* $ThBr_4$

In all cases the number of refined parameters was 10. N_{obs} is the number of contributing reflections (note that this number is selected by each program following, in general, different criteria). S is the goodness of fit and Δ/σ the maximum shift/e.s.d. after the last cycle of refinement.

	N_{obs}	w	R (%)	wR (%)	S	Δ/σ
Commensurate structure at 100 K						
XRAY system	162	$\sigma^{-2}(F)$	1.7	1.4	2.36	0.05
*SHELX*76	154	$[\sigma^2(F) + 0.000249F^2]^{-1}$	1.6	1.6	1.05	0.5
Average structure						
XRAY system	430	$\sigma^{-2}(F)$	2.4	1.7	2.83	0.08
*SHELX*76	410	$[\sigma^2(F) + 0.000048F^2]^{-1}$	2.3	2.0	2.07	0.3
MSR	389	$\sigma^{-2}(F)$	2.0	1.7	2.95	0.007

* Lists of structure factors of the basic, average and IC structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55720 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

significant. In Table 2 the approximate values extracted from Fig. 5 of Currat, Bernard & Delamoye (1986) are also included for comparison.

It can be seen from Table 2 that the elements β_{11}^{Th}, β_{22}^{Th} and β_{22}^{Br} of the atomic thermal tensors show an almost linear behaviour with the temperature when passing from the parent to the average structure. However, the rest of the diagonal elements of Th and Br atoms suffer a slighter decrease (for β_{33}^{Th} and β_{33}^{Br}) or, for β_{11}^{Br}, a noticeable increase. This latter effect was expected to occur in the average structure as its determination with the use of standard structure-factor formulae implies that the effect of the static modulation is mimicked by a spurious contribution of the static modulation to the atomic DWFs. Thus, thermal tensor elements of an average structure determined as above cannot, in general, be taken as 'thermal'. In the present case, the values indicate that the direction along which the main static displacement occurs is **a**, while the abnormally high elements, β_{33}^{Th} and β_{33}^{Br}, indicate a small but incipient additional modulated displacement of both Th and Br atoms along the *c* axis.

Each Th atom is surrounded by eight Br atoms arranged at the apices of two distorted tetrahedra (see Fig. 1) having the symmetry of the Th site. These tetrahedra constitute the first and second coordination shells of the Th^{4+} ions. The radii of these two shells at 100 K (55 K) are 2.8678 (6) Å [2.8686 (4) Å] and 3.0738 (6) Å [3.0714 (4) Å], respectively. A librational analysis of the thermal motion of Br atoms in terms of **T**, **L** and **S** tensors (Schomaker & Trueblood, 1968) using the obtained thermal tensors shows that each tetrahedron behaves, on the average, as a rigid body rotating around the *c* axis.

This qualitative result is valid in both basic and average structures, the only important difference being the mean-squared amplitudes of such rigid

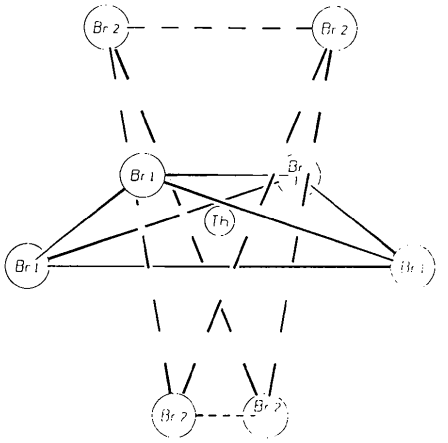

Fig. 1. *SCHAKAL88* (Keller, 1988) plot of the two first tetrahedral coordination shells of the Th^{4+} ion.

Table 4. *Elements of the superspace group* $P^{I4_1/amd}_{s\,1\,s1}$

Origin at 2/*m*. Along the internal space origin at *I*. The wavevector is $\mathbf{q}^* = \alpha\mathbf{c}^*$.

Lattice generators

$\{E\|100\ 0\}$	$\{E\|010\ 0\}$	$\{E\|001\ -\alpha\}$	$\{E\|\frac{111}{222}\ -\frac{1}{2}\alpha\}$

Rotational elements

$\{E\|000\ 0\}$	$\{C_{4z}^{+}\|\frac{313}{444}\ -\frac{3}{4}\alpha+\frac{1}{2}\}$	$\{C_{4z}^{-}\|\frac{113}{444}\ -\frac{3}{4}\alpha+\frac{1}{2}\}$	$\{C_{2x}\|0\frac{1}{2}0\ 0\}$
$\{C_{2x}\|000\ \frac{1}{2}\}$	$\{C_{2y}\|0\frac{1}{2}0\ \frac{1}{2}\}$	$\{C_{2a}\|\frac{131}{444}\ -\frac{1}{4}\alpha\}$	$\{C_{2b}\|\frac{331}{444}\ -\frac{1}{4}\alpha\}$
$\{I\|000\ 0\}$	$\{S_{4z}^{-}\|\frac{131}{444}\ -\frac{1}{4}\alpha+\frac{1}{2}\}$	$\{S_{4z}^{+}\|\frac{331}{444}\ -\frac{1}{4}\alpha+\frac{1}{2}\}$	$\{\sigma_x\|0\frac{1}{2}0\ 0\}$
$\{\sigma_x\|000\ \frac{1}{2}\}$	$\{\sigma_y\|0\frac{1}{2}0\ \frac{1}{2}\}$	$\{\sigma_{da}\|\frac{313}{444}\ -\frac{3}{4}\alpha\}$	$\{\sigma_{db}\|\frac{113}{444}\ -\frac{3}{4}\alpha\}$

rotations, which are greater in the average structure. Indeed, owing to the soft-mode character of the phase transition relating the basic and the IC structures, what we are detecting in the case of the basic structure at 100 K is the strong contribution of the soft mode to the atomic Debye–Waller factors near the phase-transition temperature. Therefore, the contribution of the same mode, already frozen and with a higher amplitude, should dominate in the atomic temperature factors of the average structure at 55 K. This qualitative description of the soft-mode displacements agrees, at least in a broad sense, with the results obtained by Bernard *et al.* (1983) from the experimental knowledge of the soft-mode irreducible representation.

4. Superspace symmetry of the incommensurate structure

If it is assumed that $I4_1/amd$ is the space group of the average structure, only two different superspace groups, $P^{I4_1/amd}_{s\,1\,s1}$ and $P^{I4_1/amd}_{1\,1\,11}$ (de Wolff, Janssen & Janner, 1981), can be assigned to the IC structure of $ThBr_4$. The former implies the extinction rules: (*a*) *hklm*, $h+k+l=2n+1$; (*b*) *00lm*, $l+2m=4n+1$; (*c*) *hk*00, $h\ (k)=2n+1$; (*d*) *h*0*lm*, $m=2n+1$; (*e*) 0*klm*, $m=2n+1$; (*f*) *hhlm*, $2h+l=4n+1$.

From a practical point of view, the two superspace groups should be distinguished from rules (*d*) and (*e*), which are due to the superspace glide plane $(^{m}_{s})$. It is known from previous work (Bernard *et al.*, 1983) that no reflections of types *h*0*l*1 and 0*kl*1 were observed in neutron Weissenberg photographs at 10 K. Nevertheless, the systematic absences (*d*) and (*e*) are only approximately satisfied in our data set. Before the averaging, 11 satellites (of a total of 45) belonging to the reciprocal planes (*h*0*l*) and (0*kl*), weakly violated $[I \geqslant 3\sigma(I)]$ these rules. However, the superspace group $P^{I4_1/amd}_{1\,1\,11}$ can be disregarded because the superspace plane $(^{m}_{1})$ would restrict the static displacements of Br atoms lying on it to occur along the Th—Br bond and the *c* axis, in clear disagreement with what should be expected from the behaviour of the atomic thermal parameters in the average structure. Therefore, the exceptions found for the selection rules corresponding to the symmetry

element ($^{m}_{s}$) should be associated with other causes such as, for example, double diffraction (Bernard *et al.*, 1983). On the other hand, the superspace group $P^{I4_1/amd}_{s\,1\,s1}$ would be the same as that proposed by Kocinsky (1990) and Janner (1992). The representative elements of this group are given in Table 4.

5. Refinement of the incommensurate structure

5.1. *Structural parameters*

As has been mentioned, the weakness of the second-order satellites and the temperature independence of the modulation wavevector suggest that the IC static distortion of $ThBr_4$ is almost sinusoidal. In this simple case the atomic modulation functions (AMFs) describing the IC displacement field of the atom μ can be expressed as

$$u^{\mu}_{i}(v) = U^{\mu}_{i,1}\cos(2\pi v + \psi^{\mu}_{i,1}) \quad (i = x, y, z), \quad (5.1)$$

where v is a continuous parameter in the range [0,1] and U^{μ}_{i1} and ψ^{μ}_{i1} are the modulus and phase of the first-harmonic complex amplitude. These latter parameters are in general considered adjustable parameters in a structure refinement.

On the other hand, it can be shown (Pérez-Mato & Madariaga, 1990; Pérez-Mato, Madariaga & Elcoro, 1991) that the effect of amplitudons and phasons can be taken into account by means of the following AMFs for the anisotropic thermal parameters*

$$\beta^{\mu}_{ij}(v) = \beta^{\mu}_{ij,0} + \beta^{\mu}_{ij,2}\cos(4\pi v + \chi^{\mu}_{ij,2}), \quad (5.2)$$

where

$$\beta^{\mu}_{ij,0} \equiv \beta^{\mu}_{ij,h} + \beta^{\mu(0)}_{ij,2}\cos(\psi^{\mu}_{i,1} - \psi^{\mu}_{j,1}), \quad (5.3)$$

$$\beta^{\mu}_{ij,2} \equiv \pi^2 U^{\mu}_{i,1} U^{\mu}_{j,1}\{\langle\delta\varphi^2\rangle - \langle\delta\rho^2\rangle\}, \quad (5.4)$$

$$\beta^{\mu(0)}_{ij,2} \equiv \pi^2 U^{\mu}_{i,1} U^{\mu}_{j,1}\{\langle\delta\varphi^2\rangle + \langle\delta\rho^2\rangle\}, \quad (5.5)$$

$$\chi^{\mu}_{ij,2} \equiv \psi^{\mu}_{i,1} + \psi^{\mu}_{j,1} + \pi, \quad (5.6)$$

$\beta^{\mu}_{ij,h}$ being an homogeneous temperature factor caused by the rest of the vibrational modes. In (5.4), (5.5) and (5.6) the modulus, ρ, of the order parameter has been normalized to be unity at 55 K and $U^{\mu}_{i,1}$ is to be introduced in relative units. Notice that $\langle\delta\varphi^2\rangle$ and $\langle\delta\rho^2\rangle$ are the only unknown additional parameters to be fitted in a structural model that includes the effect of phasons and amplitude modes on the atomic DWF. Nevertheless, the natural (although highly correlated) parameters to refine should be $\beta^{\mu}_{ij,0}$, $\beta^{\mu}_{ij,2}$ and $\chi^{\mu}_{ij,2}$. An important point is that, according to (5.6), the phase, $\chi^{\mu}_{ij,2}$, of the modulation of the thermal tensor is determined by the phases of the atomic static modulation. Hence, the theory can be directly checked by a comparison of the refined values of $\psi^{\mu}_{i,1}$ and $\chi^{\mu}_{ij,2}$.

5.2. *Symmetry restrictions of the structural parameters*

Because of the high symmetry (at least for Th atoms) of the atomic sites occupied by the independent atoms, the corresponding AMFs are strongly restricted and therefore, the number of adjustable parameters is very limited. Thus, the invariance of the AMFs [(5.1)] under the superspace transformations of each atomic site implies for the positional parameters:

(n odd)

$$U^{\mathrm{Th}}_{i,n} = 0, \qquad i = x, y, z,$$

$$U^{\mathrm{Br}}_{x,n} \neq 0, \quad \psi^{\mathrm{Br}}_{x,n} = \text{arb.}, \quad U^{\mathrm{Br}}_{i,n} = 0, \qquad i = y, z;$$

(n even)

$$U^{\mathrm{Th}}_{z,n} \neq 0, \quad \psi^{\mathrm{Th}}_{z,n} = \pm\pi/2, \quad U^{\mathrm{Th}}_{i,n} = 0, \qquad i = x, y,$$

$$U^{\mathrm{Br}}_{x,n} = 0, \quad U^{\mathrm{Br}}_{i,n} \neq 0, \quad \psi^{\mathrm{Br}}_{i,n} = \text{arb.}, \qquad i = y, z;$$

and for the thermal parameters:

(n odd)

$$\text{Th}: \quad \begin{pmatrix} 0 & \beta_{12,n} & 0 \\ \beta_{12,n} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \begin{pmatrix} - & 0,\pi & - \\ 0,\pi & - & - \\ - & - & - \end{pmatrix}$$

(Amplitudes | Phases)

$$\text{Br}: \quad \begin{pmatrix} 0 & \beta_{12,n} & \beta_{13,n} \\ \beta_{12,n} & 0 & 0 \\ \beta_{13,n} & 0 & 0 \end{pmatrix} \quad \begin{pmatrix} - & \chi_{12,n} & \chi_{13,n} \\ \chi_{12,n} & - & - \\ \chi_{13,n} & - & - \end{pmatrix}$$

(Amplitudes | Phases)

(n even)

$$\text{Th}: \quad \begin{pmatrix} \beta_{11,n} & 0 & 0 \\ 0 & \beta_{11,n} & 0 \\ 0 & 0 & \beta_{33,n} \end{pmatrix} \quad \begin{pmatrix} \chi_{11,n} & - & - \\ - & -\chi_{11,n} & - \\ - & - & 0,\pi \end{pmatrix}$$

(Amplitudes | Phases)

$$\text{Br}: \quad \begin{pmatrix} \beta_{11,n} & 0 & 0 \\ 0 & \beta_{22,n} & \beta_{23,n} \\ 0 & \beta_{23,n} & \beta_{33,n} \end{pmatrix} \quad \begin{pmatrix} \chi_{11,n} & - & - \\ - & \chi_{22,n} & \chi_{23,n} \\ - & \chi_{23,n} & \chi_{33,n} \end{pmatrix}$$

(Amplitudes | Phases)

A dash (–) means that the phase corresponding to a null amplitude is undefined. $\chi^{\mu}_{ij,n}$ is, by extension of the notation in (5.2), the phase of a term $\beta^{\mu}_{ij,n}\cos(2\pi n v + \chi^{\mu}_{ij,n})$ in the AMF of the thermal parameter β^{μ}_{ij}. Note that when $n = 0$, $\chi^{\mathrm{Th}}_{11,0} = -\chi^{\mathrm{Th}}_{22,0} = 0$ and the normal space-symmetry restrictions for this site symmetry are recovered. It is also worth noting that superspace symmetry forbids all odd harmonics, particularly the first one, of the most relevant elements of the atomic thermal tensors. Moreover,

* The β form for the anisotropic thermal tensors has been chosen because it is commonly used in the refinement programs for modulated structures and, therefore, favours a direct comparison with the results obtained.

the first harmonic of the static structural modulation is symmetry restricted to displacements of the Br atoms along the **a** direction. Therefore, according to (5.2)–(5.6), it should be expected that in a pure sinusoidal regime only the modulation of β_{11}^{Br} is non-zero, given by a second harmonic of the form (5.2). In a more general regime, we can still expect the modulation of β_{11}^{Br} to be predominant, while the symmetry-allowed modulation of other thermal-tensor components should be a weaker second-order effect. Consequently, in the refinement we have only introduced $\beta_{11,2}^{Br}$ and $\chi_{11,2}^{Br}$ as non-zero adjustable parameters, to account for modulation effects on the thermal factor, while the rest of the thermal-tensor components of both atoms have been taken as homogeneous.

6. Results and discussion

The refinement was carried out with the program *MSR* (Paciorek & Uszynski, 1987). Statistical weights $[\sigma^{-2}(F_o)]$ were used first. During the whole process a small damping factor was used to avoid divergence due to the correlation between thermal and positional parameters. In addition, an extinction parameter and an overall scale factor were also refined. The final parameters describing the static atomic displacement fields are in accordance with the estimates of Currat, Bernard & Delamoye (1986). The results obtained indicate that the refined value of $\chi_{11,2}^{Br}$ ($\chi_{11,2}^{Br}/2\pi \simeq 0.8$) verifies almost exactly the theoretical prediction given in (5.6) ($\chi_{11,2}^{Br}/2\pi = 2\psi_{x,1}^{Br} + \pi = 0.884$) if, as is normally expected, the effect of phase fluctuations overcomes that due to amplitude modes. Nevertheless, both additional parameters, $\chi_{11,2}^{Br}$ and $\beta_{11,2}^{Br}$, appear to be affected by very high standard deviations. The reason can be easily understood if the structure factor corresponding to the IC structure is written explicitly,

$$F(\mathbf{H}) = \sum_{\mu=1}^{s} f^{\mu}(H) g^{\mu}(\mathbf{H}) \exp[i2\pi(\mathbf{H}\cdot\mathbf{r}_0^{\mu})] \times \exp(-\widetilde{\mathbf{H}}\beta_0^{\mu}\mathbf{H}), \quad (6.1)$$

where $\mathbf{H} \equiv (h_1, h_2, h_3, h_4) = h_1\mathbf{a}^* + h_2\mathbf{b}^* + h_3\mathbf{c}^* + h_4\mathbf{q}$, μ runs over all the atoms, located at $\mathbf{r}_0^{\mu}$, within the average unit cell, and $\widetilde{\mathbf{H}}$ means the transposed vector of **H**. Within the refined model $\boldsymbol{\beta}_0^{\mu} = \boldsymbol{\beta}_h^{\mu}$, except for $\beta_{11,0}^{Br}$. The atomic modulation factors $g^{\mu}(\mathbf{H})$ would include the effect of the AMFs $\mathbf{U}(v)$ and $\boldsymbol{\beta}(v)$ given by (5.1), (5.2) and (5.4),

$$g^{\mu}(\mathbf{H}) = \int_0^1 dv \exp\{i2\pi[\mathbf{H}\cdot\mathbf{u}^{\mu}(v) + h_4 v]\} \times \exp[-\sum_{ij=1}^{3} h_i \beta_{ij,2}^{\mu} h_j \cos(4\pi v + \chi_{ij,2}^{\mu})]. \quad (6.2)$$

In this simple case where the positions of Th atoms are unmodulated and the AMF of Br atoms affects only one direction,* we have

$$g^{Th}(\mathbf{H}) = \begin{cases} 1 & \text{if } h_4 = 0, \\ 0 & \text{if } h_4 \neq 0, \end{cases} \quad (6.3)$$

$$g^{\mu}(\mathbf{H}) = g^{Br}(\mathbf{H}) = \int_0^1 dv \exp\{i2\pi[h_1 u_x^{Br}(v) + h_4 v]\} \times \exp[-h_1^2 \beta_{11,2}^{Br} \cos(4\pi v + \chi_{11,2}^{Br})]. \quad (6.4)$$

With substitution in (6.4) of $u_x^{Br}(v)$ and $\beta_{11}^{Br}(v)$ as given by (5.1) and (5.2) and use of the Auger–Jacobi expansions in terms of Bessel functions,

$$\exp(ix\cos\varphi) = \sum_{m=-\infty}^{\infty} J_m(x) \exp[im(\varphi + \pi/2)], \quad (6.5)$$

$$\exp(x\cos\varphi) = \sum_{m=-\infty}^{\infty} I_m(x) \exp(im\varphi), \quad (6.6)$$

$g^{Br}(\mathbf{H})$ can be expressed, with only the most important terms of the above relationships retained, as

$$g_0^{Br}(\mathbf{H}) \simeq g_{0,sin}^{Br}(\mathbf{H})\{I_0(h_1^2\beta_{11,2}^{Br}) + 2[J_2(2\pi h_1 U_{x,1}^{Br}) I_1(h_1^2\beta_{11,2}^{Br})/J_0(2\pi h_1 U_{x,1}^{Br})] \times \cos(2\psi_{x,1}^{Br} - \chi_{11,2}^{Br})\} \quad (6.7)$$

for main reflections,

$$g_{\pm 1}^{Br}(\mathbf{H}) \simeq g_{\pm 1,sin}^{Br}(\mathbf{H})\{I_0(h_1^2\beta_{11,2}^{Br}) - I_1(h_1^2\beta_{11,2}^{Br}) \times \exp[\pm i(2\psi_{x,1}^{Br} - \chi_{11,2}^{Br})]\} \quad (6.8)$$

for first-order satellites and

$$g_{\pm 2}^{Br}(\mathbf{H}) \simeq g_{\pm 2,sin}^{Br}(\mathbf{H})\{I_0(h_1^2\beta_{11,2}^{Br}) + [J_0(2\pi h_1 U_{x,1}^{Br}) I_1(h_1^2\beta_{11,2}^{Br})/J_2(2\pi h_1 U_{x,1}^{Br})] \times \exp[\pm i(2\psi_{x,1}^{Br} - \chi_{11,2}^{Br})]\} \quad (6.9)$$

for second-order satellites. $g_{\pm h_4,sin}^{Br}$ is the normal atomic modulation factor of Br in the sinusoidal regime when $\beta_{11,2}^{Br} = 0$,

$$g_{\pm h_4,sin}^{Br} = J_{\mp h_4}(2\pi h_1 U_{x,1}^{Br}) \exp[\mp i h_4(\psi_{x,1}^{Br} + \pi/2)]. \quad (6.10)$$

Notice that whereas the phase $\psi_{x,1}^{Br}$ of the displacement field is only determined by satellites, $\beta_{11,2}^{Br}$ and $\chi_{11,2}^{Br}$ appear in the expressions of the structure factor for every reflection. As a general result, the reflections most affected by the thermal-tensor modulation and, hence, optimal to determine accurately $\beta_{11,2}^{Br}$ and $\chi_{11,2}^{Br}$, are those second-order satellites having a medium-low h_1 index, *i.e.* those which

* We will only write explicitly the atomic modulation factors of the independent atoms.

should be, in general, more easily measured. Our data set lacks second-order satellites; therefore, according to (6.7) and (6.8), first-order satellites will dominate in the determination of $\chi^{Br}_{11,2}$ at low Bragg angles. However, the ratio $J_2(z)/J_0(z)$ reaches values greater than unity at higher angles and, as a consequence, the influence of first-order satellites in determining $\chi^{Br}_{11,2}$ will be overcome by that of main reflections. Anyway, it is worth noting that using only main reflections and first-order satellites [see (6.7) and (6.8)], the influence of phasons and amplitudons appears as a second-order correction. Thus, in the absence of second-order satellites, $\beta^{Br}_{11,2}$ and $\chi^{Br}_{11,2}$ can be only poorly determined.

To check that the least-squares minimum at $\chi^{Br}_{11,2} \simeq 0.8$ (hereafter we will denote by $\chi^{Br}_{11,2}$ its normalized value $\chi^{Br}_{11,2}/2\pi$) was significant, a series of refinements were performed with $\chi^{Br}_{11,2}$ fixed at arbitrary values and the rest of the parameters varied. Indeed, for $\chi^{Br}_{11,2}$ ranging between 0.2 and 0.6, it was also necessary to restrict the value of $\beta^{Br}_{11,2}$ for the refinement to converge. This indicated, in agreement with the standard deviation of $\chi^{Br}_{11,2}$, that the true minimum for $\chi^{Br}_{11,2}$ lay in the interval (0.5, 1.2) (modulo 1). Nevertheless, for the sake of completeness, the whole range [0,1) was calculated and, in the case of $\chi^{Br}_{11,2}$ values in the unstable region, $\beta^{Br}_{11,2}$ was fixed to the value obtained by least squares at $0.5 + \chi^{Br}_{11,2}$ (modulo 1).

The results were rather surprising because the analysis of the wR factors for first-order satellites (wR_1) showed behaviour insensitive to $\chi^{Br}_{11,2}$, whereas wR for main (wR_0) and all reflections (wR_{all}, which is expected to be dominated by the former) exhibited a marked minimum centred at about $\chi^{Br}_{11,2} = 0.8$. Furthermore, a remarkable minimum of wR_1 appeared at $\chi^{Br}_{11,2} \simeq 0.3$.

At this point, experimental data were carefully checked. Surprisingly, although the ratio between $[\sum F_{obs}/n_{refl}]_{main}$ and $[\sum F_{obs}/n_{refl}]_{sat}$ was about 5.2, the equivalent weighted ratio was 0.77. This indicated a clear overestimation of the satellite weights. Moreover, five of 54 satellites had a weight twice that of the most weighted main reflection and their contribution to wF_{obs} represented 80% of the same summation for the rest of satellites. It means that those five reflections drive the refinement process to obtain for them an $|F_{obs} - F_{calc}|$ difference as low as possible. This fact would cause a minimum around $\chi^{Br}_{11,2} = 0.3$, since the change in $\chi^{Br}_{11,2}$ from 0.8 to 0.3 implies a change of sign within the term that includes $\beta^{Br}_{11,2}$ in (6.8) and, therefore, a small but apparently important improvement of $|F_{obs} - F_{calc}|$ for these most weighted satellites.

On the other hand, an analysis of the consistency of weights by means of normal-probability plots (Abrahams & Keve, 1971) showed an unbiased normal error distribution for both main reflections and satellites when considered separately. Nevertheless, the relative weight of the satellites was unusually large, even when, as we knew from the experimental conditions, the counting time for satellites was three times larger than that used for main reflections. Roughly speaking, this would imply that the statistical weight of one satellite should be approximately three times the weight assigned to a main reflection having the same intensity.

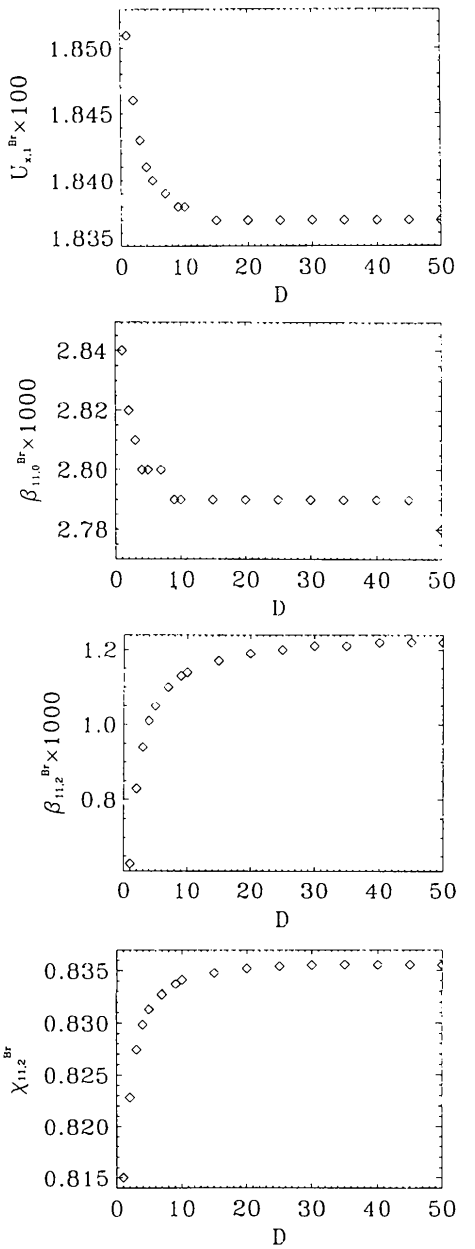

Fig. 2. Graphical representation of the variation suffered by those parameters that are affected by D (see text).

Table 5. *Final parameters describing the incommensurate structure of* $ThBr_4$ *at* 55 K

Thermal parameters are multiplied by 10^5. Estimated standard deviations are given in parentheses. Again the extradiagonal element $\beta^{Br}_{23,h}$ has been omitted for simplicity.

Th	x_0	y_0	z_0	$\beta_{11,h}$	$\beta_{22,h}$	$\beta_{33,h}$
	0	$\frac{3}{4}$	$\frac{1}{8}$	23 (2)	23 (2)	68 (4)
Br	x_0	y_0	z_0	$\beta_{11,0}$	$\beta_{22,h}$	$\beta_{33,h}$
	0	0.56426 (6)	0.79771 (3)	278 (17)	72 (3)	119 (3)
	$U_{x,1}$	$\psi_{x,1}$ (/2π)	$\beta_{11,2}$	$\chi_{11,2}$ (/2π)		
	0.0184 (4)	0.192 (11)	119 (210)	0.835 (300)		

At this point we began a systematic study of the influence on our results of the weighting ratio between satellites and main reflections. The weights of satellites were arbitrarily divided by a factor, D, of increasing value. For each D value all parameters were refined ('free refinement'). Then a curve of wR *versus* $\chi^{Br}_{11,2}$ was obtained in the way indicated above. The main conclusions that can be extracted from this study are as follows.

(i) The parameters affected by the value of D are $U^{Br}_{x,1}$, $\beta^{Br}_{11,0}$, $\beta^{Br}_{11,2}$ and $\chi^{Br}_{11,2}$ (see Fig. 2). However, their variation is always within their standard deviation. Only the mean value of $\beta^{Br}_{11,2}$ (which is effectively undetermined) exhibits an important increase with D. Now, from (6.8), it is easy to understand the insensitivity of wR_1 to $\chi^{Br}_{11,2}$ when $D = 1$ [*i.e.* when the 'true' $\sigma(F)$ are used in the weighting scheme]; $\beta^{Br}_{11,2}$ is so low that the term containing $\chi^{Br}_{11,2}$ in (6.8) is almost irrelevant. Note that for $D \geq 9$ all parameters are constant. Nevertheless, and as a reference, $D \simeq 25$ implies that reflections with the same intensity are equally weighted and $7 \leq D \leq 9$ would reflect a weighting scheme in accordance with the average time of measurement spent in each reflection. Fig. 2 should really be considered as the graphical representation of the most important correlations occurring during the least-squares procedure. Parameters corresponding to $D = 25$ have been chosen as final results in Table 5. The corresponding final R factors (weighted R factors) were 0.0193 (0.0154), 0.0186 (0.0153) and 0.045 (0.0285) for all, main and first-order satellites, respectively.*

(ii) The three-dimensional surfaces constructed from the above results [see Figs. 3(*a*), 3(*b*) and 3(*c*)] show on the one hand the expected behaviour from (5.6); Figs. 3(*a*)–3(*c*) show deep although rather broad minima centred at $\chi^{Br}_{11,2} \simeq 0.8$ for every D. Also, the value reached by $\chi^{Br}_{11,2}$ during the 'free refinements' [Figs. 4(*a*)–4(*c*)] is independent of the weighting scheme. On the other hand, Figs. 3(*b*) and 3(*c*) show an abrupt increase of wR_0 and wR_{all} in the neighbourhood of $D = 1$, indicating that the associated weight relations between main reflections and satellites are essentially wrong. The subsidiary minimum for satellites, at $\chi^{Br}_{11,2} \simeq 0.3$, is also present for every D. Its relative depth decreases as the influence of the most weighted satellites is lowered by the rest of the reflections.

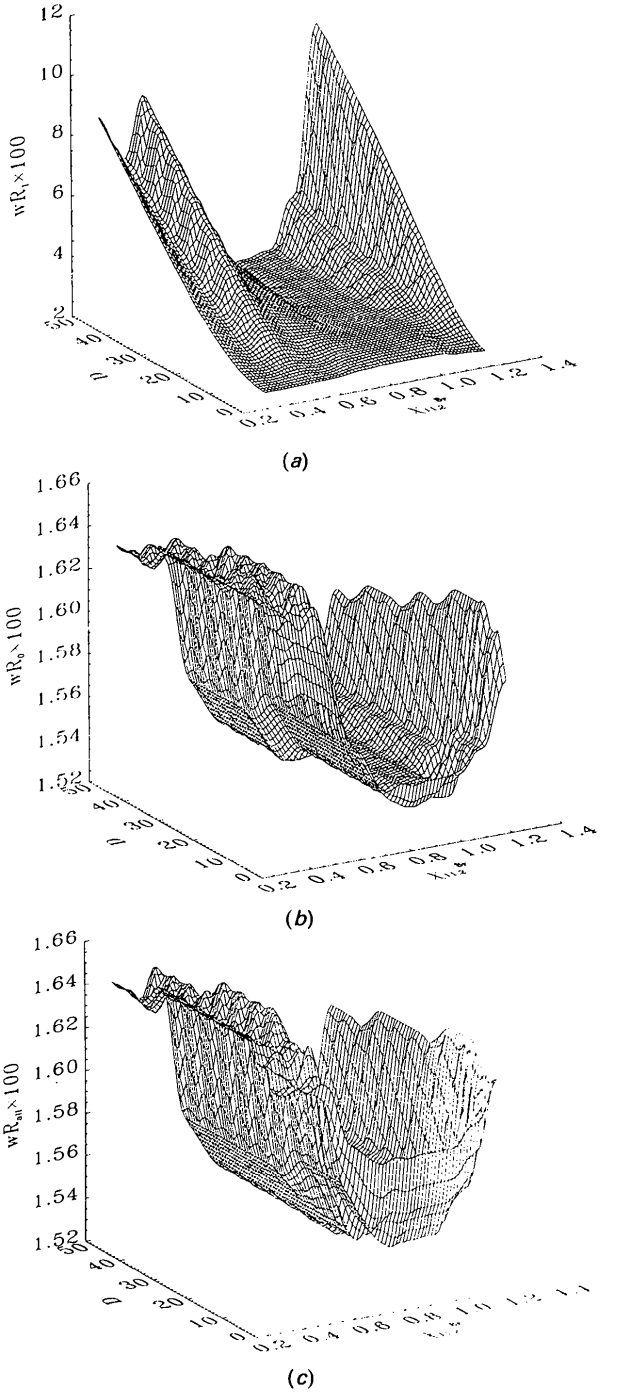

Fig. 3. Three-dimensional plots of (*a*) wR_1, (*b*) wR_0 and (*c*) wR_{all} as functions of $\chi^{Br}_{11,2}$ and D (see text).

* See deposition footnote.

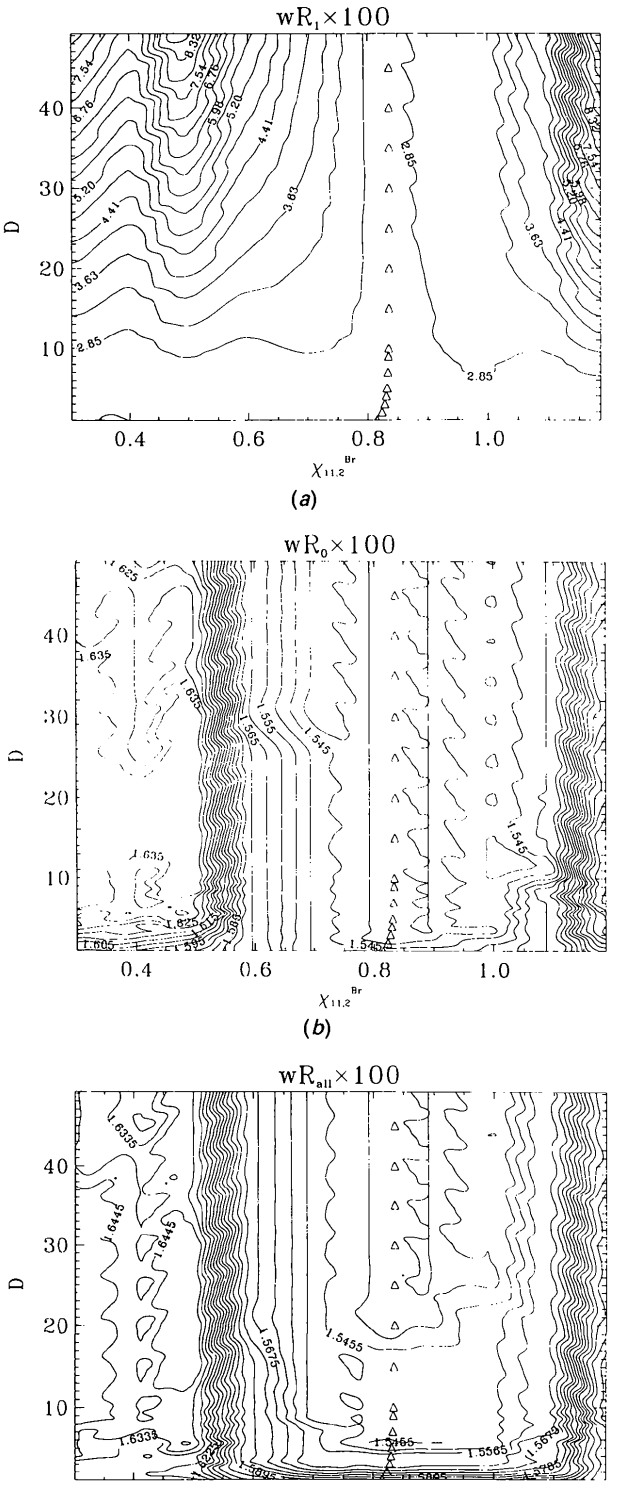

Fig. 4. Contour maps of (*a*) wR_1, (*b*) wR_0 and (*c*) wR_{all} corresponding to Figs. 3(*a*), 3(*b*) and 3(*c*), respectively. Triangles indicate the values reached by $\chi^{Br}_{11,2}$ during the 'free refinements'.

(iii) Fig. 3(*a*) shows clearly that the indicator which is the most sensitive to $\chi^{Br}_{11,2}$ (at least for D values greater than 10) is wR_1. Hence, it could be used as a good estimator of the importance of modulating the atomic thermal parameters. In fact, whatever the value of D, when a structural model without AMFs for the atomic temperature factors is refined, the R factors* obtained (weighted R factors) for all [0.0197 (0.0156)] and main reflections [0.0189 (0.0153)] are only slightly higher than those of our final model in Table 5. However, wR_1 [0.0504 (0.0403)] is remarkably higher, as could be expected from the very high boundaries shown by this partial agreement factor in Fig. 3(*a*).

The contribution, $\beta^{Br(0)}_{11,2}$, of phase and amplitude thermal fluctuations to the homogeneous term in the AMF of $\beta^{Br}_{11}(v)$ [see (5.3) and (5.5)] cannot be derived from the value obtained for $\beta^{Br}_{11,0}$, as the only reference value we have of β^{Br}_{11} in the normal phase corresponds to $T = 100$ K, only 5 K above the transition temperature and consequently strongly influenced by the soft mode. However, from the amplitude, $\beta^{Br}_{11,2}$, of the modulation of β^{Br}_{11}, with (5.4) and the assumption $\langle\delta\varphi^2\rangle \gg \langle\delta\rho^2\rangle$, an estimate of 0.3–0.4 for $\langle\delta\varphi^2\rangle$ can be obtained. This value can be compared with the approximate value that can be derived with a modified Debye model, from the observed dispersion of the phason branches reported by Bernard *et al.* (1983) and Currat, Bernard & Delamoye (1986). According to Pérez-Mato & Madariaga (1990) and for the particular case considered here,

$$\langle\delta\varphi^2(T)\rangle = [\hbar/8Nm_{Br}(U^{Br}_{x,1}a)^2] \times \int_0^\infty (d\omega/\omega)g_{ph}(\omega)[2n(\omega)+1], \quad (6.11)$$

where $U^{Br}_{x,1}$ is introduced in relative units, $n(\omega)$ is the thermal Bose population factor, N is the number of basic cells in the sample, m_{Br} is the atomic mass of Br and $g_{ph}(\omega)$ is the density of phason modes. From the neutron results of Bernard *et al.* (1983), it can be supposed that real phason modes are restricted to a sphere of small wavevectors limited by a certain cut-off value, which, with anisotropic effects neglected, can be taken to be equal for all directions. Consequently, the special normalization condition of $g_{ph}(\omega)$ will be $\int_0^\infty g_{ph}(\omega)d\omega = N_{ph}$, where N_{ph} is the number of phason modes, in the mentioned sphere, smaller than N. In a Debye model, $g_{ph}(\omega) = 3N_{ph}(\omega^2/\omega_L^3)$, where $\omega_L = v_{ph}k_L$, v_{ph} being a mean value for the slope of the phason branches. With the assumption $T \gg \theta_L \equiv \hbar\omega_L/K_B$, the usual approximation can be introduced and $\langle\delta\varphi^2\rangle$ is proportional to T,

$$\langle\delta\varphi^2(T)\rangle = 3R_{ph}\hbar^2T/4m_{Br}(U^{Br}_{x,1}a)^2K_B\theta_L^2, \quad (6.12)$$

* For comparison the bracketed R factors correspond to $D = 25$.

where $R_{ph} = N_{ph}/N$ is also given by the ratio of the volume of the sphere of phason wavevectors limited by k_L with respect to the volume of the primitive reciprocal cell. From (6.12), and with the experimental and physical constants substituted,

$$\langle \delta\varphi^2(55\ \mathrm{K})\rangle \simeq 933 R_{ph}/\theta_L^2. \qquad (6.13)$$

From the neutron experimental results (Bernard *et al.*, 1983; Currat, Bernard & Delamoye, 1986), a maximum value of $\sim 0.6\pi/a$ can be taken for k_L, while θ_L is of the order of 20 K; consequently $\langle \delta\varphi^2(55\ \mathrm{K})\rangle$ should be less than 0.26. Although the estimated value obtained from the modulation of the thermal coefficient is of the same order of magnitude, it seems too large when compared with the present calculation. However, the results are quite consistent if the uncertainties in both calculations are taken into account.

7. Concluding remarks

Within the resolution of our data set, the effect of phasons and amplitudons modulating the atomic DWF has been detected and evaluated. The value of $\chi^{Br}_{11,2}$ verifies almost exactly the theoretical prediction and agrees with the expectation that $\langle \delta\varphi^2\rangle$ is greater than $\langle \delta\rho^2\rangle$. It should be stressed that the phase relationship between $u_x^{Br}(v)$ and $\beta_{11}^{Br}(v)$ implies that the maximum atomic thermal displacements occur at those atomic sites where the static distortion is smaller. Reciprocally, minimum thermal displacements will correspond to atoms having the maximum static displacement (see Fig. 5). As the standard weights in the available data set presented some inconsistencies, a careful analysis of them had to be performed. Nevertheless, most of the refined parameters seem to be insensitive to drastic changes in the weighting scheme and, globally, the results remain unchanged. The mean value of $\beta^{Br}_{11,2}$ is comparable, in magnitude, with the rest of thermal parameters, indicating a strong contribution of phasons. It is important to remark that the modulated DWF for Br atoms has the form $\exp[-h_1^2\beta_{11}^{Br}(v)]$. This means that it affects all reflections and, owing to the direction of the modulation wavevector, is independent of h_4. Therefore, any attempt to convert these temperature factors into the conventional Overhauser PDWF formula (notice also that, by definition, the present data set would not be affected by Axe's factor) would prove impossible. A more accurate result would require the measurement, if possible, of second-order satellites and the direct refinement (with use of, for example, nonlinear constraints in the least-squares algorithm) of $\langle \delta\varphi^2\rangle$ and $\langle \delta\rho^2\rangle$.

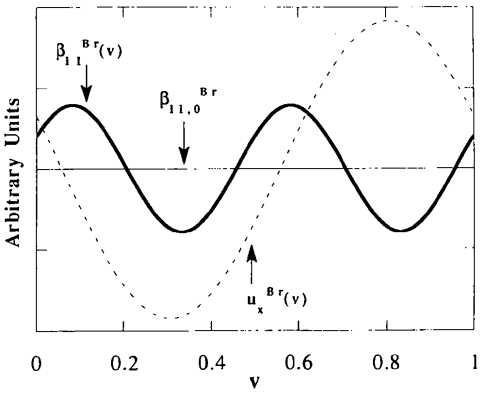

Fig. 5. Schematic representation of the phase relation existing between $\beta_{11}^{Br}(v)$ and $u_x^{Br}(v)$. $\beta_{11}^{Br}(v)$ has been drawn with use of the refined values of $\beta_{11,0}$, $\beta_{11,2}$ and $\chi_{11,2}$, listed in Table 5. The amplitude $U_{x,1}$ has been arbitrarily scaled to fit within the plot frame.

The experimental data used in this work were kindly supplied by J. Pannetier and R. Currat, from the Institut Laue–Langevin (Grenoble). One of the authors (IA) is indebted to the Basque Government for financial support. This work has been supported by the UPV/EHU project No. 063.310-E065/90.

References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A**27**, 157–165.
AXE, J. D. (1980). *Phys. Rev. B*, **21**, 4181–4190.
BERNARD, L., CURRAT, R., DELAMOYE, P., ZEYEN, C. M. E., HUBERT, S. & DE KOUCHKOVSKY, R. (1983). *J. Phys. C*, **16**, 433–456.
CHAPMAN, L. D. & COLELLA, R. (1984). *Phys. Rev. Lett.* **52**, 652–655.
CHAPMAN, L. D. & COLELLA, R. (1985). *Phys. Rev. B*, **32**, 2233–2242.
COLELLA, R. (1989). *Phys. Rev. B*, **39**, 1501–1505.
CURRAT, R., BERNARD, L. & DELAMOYE, P. (1986). *Incommensurate Phases in Dielectrics. Materials*, edited by R. BLINC & A. P. LEVANYUK. Amsterdam: North Holland.
CURRAT, R. & JANSSEN, T. (1987). *Solid State Phys.* **41**, 201–302.
EHSES, K.-H. (1985). *Jpn. J. Appl. Phys.* **24**, 793–795.
GARCÍA, A., PÉREZ-MATO, J. M. & MADARIAGA, G. (1989). *Phys. Rev. B*, **39**, 2476–2483.
JANNER, A. (1992). *Methods of Structural Analysis of Modulated Structures and Quasicrystals*, edited by J. M. PÉREZ-MATO, F. J. ZÚÑIGA & G. MADARIAGA, pp. 64–78. Singapore: World Scientific.
KELLER, E. (1988). *SCHAKAL88*. A program for the graphic representation of molecular and crystallographic models. Univ. of Freiburg, Germany.
KOCINSKI, J. (1990). *Commensurate and Incommensurate Phase Transitions*, pp. 238–240. Amsterdam: Elsevier.
MADARIAGA, G., ZÚÑIGA, F. J., PACIOREK, W. A., PÉREZ-MATO, J. M., EZPELETA, J. M. & ETXEBARRIA, I. (1990). *Ferroelectrics*, **105**, 309–314.
OVERHAUSER, A. W. (1971). *Phys. Rev. B*, **3**, 3173–3182.
PACIOREK, W. A. & KUCHARCZYK, D. (1985). *Acta Cryst.* A**41**, 462–466.
PACIOREK, W. A. & USZYNSKI, I. (1987). *J. Appl. Cryst.* **20**, 57–59.
PÉREZ-MATO, J. M. & MADARIAGA, G. (1990). *Geometry and Thermodynamics*, edited by J.-C. TOLÉDANO, pp. 405–415. New York: Plenum Press.

PÉREZ-MATO, J. M., MADARIAGA, G. & ELCORO, L. (1991). *Solid State Commun.* **78**, 33–37.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
STEURER, W. & ADLHART, W. (1983). *Acta Cryst.* B**39**, 349–355.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The *XRAY*72 system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* A**37**, 625–636.
YAMAMOTO, A. (1982). *Acta Cryst.* A**38**, 87–92.

Acta Cryst. (1993). B**49**, 254–258

Structure of *N*-(Dichlorophosphinoyl)phosphorimidic Trichloride, $Cl_3PNP(O)Cl_2$, at 100 K

BY FERDINAND BELAJ

Institut für Anorganische Chemie, Universität Graz, Schubertstrasse 1, *A*-8010 *Graz, Austria*

(*Received* 18 *June* 1992; *accepted* 4 *September* 1992)

Dedicated to Professor Dr Edgar Nachbaur on the occasion of his 60*th birthday*

Abstract

N-(Dichlorophosphinoyl)phosphorimidic trichloride, $Cl_3PNP(O)Cl_2$, $M_r = 269.22$, monoclinic, $P2_1/c$, $a = 12.573\ (5)$, $b = 19.183\ (4)$, $c = 14.985\ (4)$ Å, $\beta = 110.14\ (2)°$, $V = 3393\ (1)$ Å^3, $Z = 16$, $D_x = 2.108$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 2.02$ mm^{-1}, $F(000) = 2080$, $T = 100$ K, $R = 0.030$, $wR = 0.032$ for 4458 unique observed reflections and 325 parameters. There are four molecules in the asymmetric unit. The P—N bonds show a pronounced multiple-bond character, the P—N 'double' bonds [1.517 (3)–1.530 (3) Å] being substantially shorter than the P—N 'single' bonds [1.583 (3)–1.593 (3) Å], and the P—Cl bonds of the $P(O)Cl_2$ groups [1.998 (2)–2.018 (2) Å] are clearly longer than the P—Cl bonds of the $NPCl_3$ groups [1.956 (2)–1.978 (2) Å]. The very flexible P—N—P bond angles lie in the range 137.8 (2)–144.1 (2)°. All four molecules show approximate *cisoid* conformations with respect to their Cl—P···P—Cl and Cl—P···P—O torsion angles. The packing consists of layers normal to the monoclinic axis, each built up of two crystallographically independent molecules with similar environments. In opposition to this, the molecules in alternating layers show very different arrangements.

Introduction

N-(Dichlorophosphinoyl)phosphorimidic trichloride, the stable fundamental substance of neutral linear chlorophosphazenes, can be obtained by many different reactions (Becke-Goehring, Debo, Fluck & Goetze, 1961; Becke-Goehring & Lehr, 1961, 1963; Becke-Goehring, Mann & Euler, 1961; Becke-Goehring & Fluck, 1966; Emsley, Moore & Udy, 1971; Fluck, Hösle & Zischka, 1981). The evidence of three rotamers derived from ^{31}P NMR data (Glidewell, 1979) was disproved by semiempirical theoretical calculations (Glidewell, 1980; Glidewell, Keat & Rycroft, 1981) and by temperature-dependent ^{31}P NMR experiments (Thomas, Scheller & Grossmann, 1982). The ^{35}Cl NQR spectrum (Kaplansky, Clipsham & Whitehead, 1969) shows a line splitting presumably due to crystallographic inequivalence of the Cl atoms.

An X-ray crystal structure analysis performed at room temperature was repeated at 223 K because of an extremely high degree of thermal motion in the bridging N atoms and because of a phase transition below 223 K generating a slightly different packing arrangement (Allcock, Tollefson, Arcus & Whittle, 1985). But the results of the structure redetermination showing two molecules in the asymmetric unit are unsatisfactory, exhibiting positional disorder, very different bond lengths of equivalent bonds in the two molecules [P=O 1.453 (8) and 1.398 (10) Å, P—N 1.580 (8) and 1.53 (2) Å, P=N 1.519 (8) and 1.54 (2) Å in molecules *A* and *B*, respectively], which are unrealistic in molecule *B*, and gross violation of Hirshfeld's 'rigid-bond' postulate (Hirshfeld, 1976), in particular for the P—N bonds of molecule *B*.

As part of a continuing study of phosphazene structures, the crystal structure of the title compound was determined at 100 K. At this temperature an ordered structure was obtained with the same space-group type but with a doubled cell, more accurate structural parameters and realistic thermal parameters. The asymmetric unit consists of four molecules

0108-7681/93/020254-05$06.00