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Multipole Analysis of the Nuclear Smearing Functions in Caesium Lead Trichloride $CsPbCl_3$

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Abstract

The multipole components of the nuclear smearing function of Cl in $CsPbCl_3$ indicate significant bulging of the nuclear distribution in the plane perpendicular to the Pb–Cl connecting line away from the directions where the neighbouring Cs atoms are located. A disordering of the Cl atom into the four positions $\frac{1}{2},\pm u,0$; $\frac{1}{2},0,\pm u$ offers a possible interpretation. The application of Rietveld's profile-refinement program to the anisotropic disordered model yields $u = 0{\cdot}071$ corresponding to the displacement $r_{Cl} = 0{\cdot}40$ (5) Å and the anisotropic temperature factors $B_{11} \simeq B_{22} = 7{\cdot}3$ (2) Å^2, $B_{33} = 1{\cdot}93$ (7) Å^2. There is no indication of disordering or anharmonicity of the Cs and Pb distributions.

1. Introduction

$CsPbCl_3$ has a cubic perovskite-like structure above 320 K (Møller, 1959; Fujii, Hoshino, Yamada & Shirane, 1974; Harada, Sakata, Hoshino & Hirotsu, 1976). The space group is *Pm*3*m* with the ideal positions: Pb in 1(*a*): 000; Cs in 1(*b*): $\frac{111}{222}$; Cl in 3(*d*): $\frac{1}{2}00$; with point symmetries *m*3*m* for the Pb and Cs atoms and 4/*mmm* for Cl (Fig. 1). On the basis of the X-ray diffraction measurements Møller suggests the structure to be disordered. He proposes two models: In one model the Cs atoms are displaced into six equivalent positions along the cube edge directions and the Cl atoms into four equivalent positions along the face diagonals towards the neighbouring Cs atoms. In the other model the Cs atoms have eight equivalent positions along the body-diagonal directions towards the Pb positions and the four equivalent positions of the Cl atoms are now displaced parallel to the cube edges in the ClCs plane.

Harada *et al.* (1976) reinvestigated the structure at 328 K by the neutron diffraction technique using a single crystal. They concluded that the structure was represented best by the perovskite model with anomalously large thermal vibrations for the Cs and Cl atoms. Furthermore they suggested that it would be necessary to include the effect of anharmonic terms for their thermal vibrations. Sakata, Harada, Rouse & Cooper (1978) have recently determined the potential coefficients in a one-body potential approximation and concluded that the Cs and Cl atoms are located in very strong anharmonic potentials whereas a harmonic potential is adequate for the Pb atom. However, the theoretical models, which deal with displacive structural phase transitions caused by a soft mode, imply that the average structure of the high-temperature phase is disordered with the atoms occupying the sites

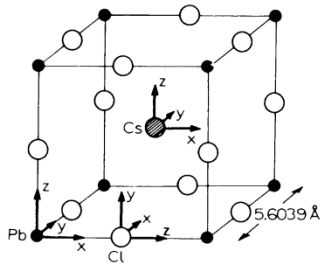

Fig. 1. The local coordinate axes of the atoms in cubic $CsPbCl_3$. The axes of the unit cell coincide with those of the Pb atom.

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obtained by operating on the low-temperature structure with the high-temperature symmetry (*e.g.* Comès, Lambert & Guinier, 1970).

The purpose of this study is to investigate the nuclear distributions of the atoms in $CsPbCl_3$. Particular attention is paid to the possibility of interpreting the large r.m.s. amplitude of the Cl atom in terms of disordering. We apply the site-symmetric multipole analysis of Kurki-Suonio (1977). Each multipole component of each atom is calculated and interpreted separately on the basis of the experimental structure amplitudes. In this way the experimental information is expressed in terms of independent statements which can be judged separately and will not be obscured by complex correlation problems. The applications to the study of molecular orientation in NH_4Cl (Kurki-Suonio, Merisalo, Vahvaselkä & Larsen, 1976) and ND_4NO_3 (Ahtee, Kurki-Suonio, Lucas & Hewat, 1979) indicate that the method will be able to reveal also the nature of the possible disorder or anharmonicity of the atoms.

2. Data collection and profile refinement

Neutron diffraction measurements were made on the powder diffractometer (D1A) at the high-flux reactor in the ILL (Grenoble) using the wavelength 1·9073 Å. A sample of 20 g was packed in a thin-walled vanadium can of diameter 16 mm. The counter bank consisting of ten ^{3}He high-pressure counters (Hewat & Bailey, 1976) was swept through the 2θ region 0...160° in steps of 0·05°.

The diffraction pattern measured at 331 K consists of 36 nonequivalent reflections; 28 of them occur at different θ values. The neutron scattering lengths used were: $g_{Pb} = 9{\cdot}40$ fm, $g_{Cs} = 5{\cdot}42$ fm and $g_{Cl} = 9{\cdot}58$ fm. Rietveld's (1969) profile-refinement technique modified by Hewat (1973) to include anisotropic temperature factors was used in separating the reflections.

Table 1. *Temperature factors of cubic* $CsPbCl_3$ *(a) with the ideal perovskite structure obtained by using Rietveld's profile-refinement technique on powder diffraction data and (b) obtained by using Rietveld's profile-refinement technique when the starting model is the disordered model* 2

	(*a*)	(*b*)
Temperature factors		
B(Cs)	6·09 (8) Å^2	6·04 (7) Å^2
B(Pb)	1·94 (3)	1·87 (3)
B_{11}(Cl) = B_{22}(Cl)	15·06 (9)	7·32 (21)
B_{33}(Cl)	1·99 (7)	1·93 (7)
Position parameter x of Cl		0·072 (8)
Lattice parameter a	5·6039 (6) Å	5·6039 (6) Å
Reliability factors		
R_N	3·9%	2·4%
R_P	9·7	7·8

Eleven parameters were refined; six of these characterize the measuring system: the counter zero-point, three half-width parameters, the scale factor and the asymmetry parameter; the other five parameters are connected with the structural properties: the lattice constant, the isotropic temperature factors of the Pb and Cs atoms and the two parameters of the axial temperature factor of Cl. The results of the refinement are collected in Table 1. The reliability factors are calculated from the equations $R_P = 100 \sum_i |y_{i,\mathrm{obs}} - Sy_{i,\mathrm{calc}}| / \sum_i y_{i,\mathrm{obs}}$%, $R_N = 100 \sum |I_{\mathrm{obs}} - SI_{\mathrm{calc}}| / \sum I_{\mathrm{obs}}$%, where y_i is the intensity at an angle θ_i in the diffraction pattern and summation is made over all the measured positions i, S is the scale factor and I the integrated intensity of the reflection. The inclusion of the anisotropy in the thermal vibration of the Cl atom reduced the R value drastically from $R_N = 19{\cdot}4$ to 3·90%.

3. Direct multipole analysis

The experimental information about the nuclear density distribution $s(\mathbf{r})$ is contained in the neutron structure amplitudes, the coefficients G_j of the expansion

$$s(\mathbf{r}) = \frac{1}{V} \sum_j G_j \exp(-2\pi i \mathbf{S}_j . \mathbf{r}). \tag{1}$$

As usual $s(\mathbf{r})$ is represented as a superposition of nuclear smearing functions τ_n

$$s(\mathbf{r}) = \sum s_n(\mathbf{r} - \mathbf{r}_n) = \sum g_n \tau_n(\mathbf{r} - \mathbf{r}_n), \tag{2}$$

where $\int \tau_n(\mathbf{r})\, \mathrm{d}^3 r = 1$, g_n is the neutron scattering length and $\mathbf{r}_n$ the equilibrium nuclear position of the nth nucleus. The disordering or anharmonicity of the nth atom will manifest itself in the shape of $s_n(\mathbf{r})$.

In the multipole analysis the distribution $s_n(\mathbf{r})$ of an atom and its Fourier transform $\sigma_n(\mathbf{S})$ are expressed as site-symmetric multipole expansions (Kurki-Suonio, 1977)

$$s_n(\mathbf{r}) = \sum_{lmp} s^n_{lmp}(r)\, y_{lmp}(\theta,\varphi) \tag{3}$$

$$\sigma_n(\mathbf{S}) = \sum_{lmp} \sigma^n_{lmp}(S)\, y_{lmp}(\theta_S,\varphi_S), \tag{4}$$

where r,θ,φ and S,θ_S,φ_S are the spherical coordinates in real and reciprocal spaces, respectively, and y_{lmp} are site-symmetric spherical harmonics $y_{lmp} = y_{lm\pm} = P_l^m(\cos\theta)^{\cos(m\varphi)}_{\sin(m\varphi)}$, $m \leq 1$, normalized to the maximum value 1 and having l,m,p chosen according to the site symmetry. In the case of cubic symmetries corresponding series in terms of the cubic harmonics $K_{l\mu}$ should be used.

If the nuclear distribution s_n is well separated from the neighbouring distributions the entire distribution of

the nucleus concerned is contained within a sphere of radius R_n. Then the radial scattering factors $\sigma^n_{lmp}(S)$ in equation (4) are obtained (Kurki-Suonio, 1967) from the expression

$$\sigma^n_{lmp}(S) = \frac{16\pi^2 R_n^3}{V A_{lmp}} \times \sum_j G_j \frac{x j_{l+1}(x)\, j_l(x_j) - x_j\, j_{l+1}(x_j)\, j_l(x)}{x^2 - x_j^2} y_{lmp}(\theta_j, \varphi_j), \quad (5)$$

where $x = 2\pi R_n S = 4\pi R_n \sin\theta/\lambda$, $x_j = 2\pi R_n S_j$, $j_l(x)$ is the spherical Bessel function of order l, $A_{lmp} = \int y^2_{lmp}\, d\Omega$. S_j, θ_j, φ_j are the spherical coordinates of the jth reciprocal-lattice vector and the structure factors G_j are phased with respect to the ideal atomic position.

In the direct multipole analysis the series (5) is applied as a difference series with $\Delta G_j = G_j^{\rm obs} - G_j^{\rm theor}$ as coefficients. The experimental structure factors $G_j^{\rm obs}$ are now obtained as a result of the profile refinement. Through corrections included in the refinement procedure they, thus, depend on the model used. This dependence can be controlled by using different models. It is, however, of second order, *cf.* Ahtee *et al.* (1979), and has no essential effect on the results. For theoretical structure factors $G_j^{\rm theor}$ we define a reference

Table 2. *The structure factors of* $CsPbCl_3$

The experimental and theoretical structure factors $G^{\rm obs,1}$ and $G^{\rm theor,1}$ are based on the profile refinement of the ideal cubic perovskite structure including the anisotropic vibration of the Cl atom. The structure factors $G^{\rm obs,2}$ and $G^{\rm theor,2}$ are based on the refinement starting from the disordered model 2, where the Pb and Cs atoms with harmonic thermal behaviour are at the ideal perovskite positions and the Cl atom with anisotropic thermal vibration is disordered.

hkl	$\sin\theta/\lambda$	$G^{\rm obs,1}$	$G^{\rm theor,1}$	$G^{\rm obs,2}$	$G^{\rm theor,2}$
100	0.08922	1.17512	1.16581	1.19002	1.18243
110	0.12618	0.46567	0.48426	0.47160	0.48103
111	0.15454	-1.80010	-1 79691	-1.82307	-1.83466
200	0.17845	3.44464	3.41553	3.48862	3.46037
210	0.19951	1.19527	1.18481	1.21053	1.19159
211	0.21855	0.89845	0.93403	0.90991	0.91797
220	0.25236	2.71090	2.67906	2.74551	2.72711
300	0.26767	0.29344	0.28821	0.32323	0.32310
221	0.26767	1.11379	1.09394	1.12622	1.12577
310	0.28215	0.32543	0.37066	0.32959	0.35609
311	0.29592	-0.75481	-0.74707	-0.76445	-0.77362
222	0.30908	2.09328	2.11785	2.11991	2.13496
320	0.32170	0.45220	0.47347	0.45797	0.45845
321	0.33384	0.67390	0.64880	0.68250	0.66333
400	0.35689	2.00130	2.00897	2.02685	2.02928
410	0.36788	1.12084	1.13137	1.14740	1.13689
322	0.36788	0.54035	0.54428	0.52106	0.51629
411	0.37854	1.30055	1.27798	1.33029	1.31316
330	0.37854	0.49291	0.48436	0.42384	0.41838
331	0.38892	0.	-0.12462	0.	-0.09527
420	0.39902	1.58771	1.57548	1.60798	1.57648
421	0.40887	0.96644	0.92378	0.97878	0.96924
332	0.41850	0.56229	0.61020	0.56947	0.60792
422	0.44710	1.22147	1.26688	1.23707	1.22370
500	0.44612	-0.06495	-0.07153	-0.08184	-0.08463
430	0.44612	0.59594	0.65643	0.60306	0.62360
510	0.45495	0.22178	0.20623	0.19724	0.19609
431	0.45495	0.91618	0.85194	0.93099	0.92557
511	0.46362	-0.16052	-0.11760	-0.10837	-0.09738
333	0.46362	0.25274	0.18530	0.33103	0.29749
520	0.48048	0.12756	0.14321	0.09062	0.09533
432	0.48048	0.52899	0.59385	0.53969	0.56779
521	0.48870	0.35788	0.37475	0.36246	0.38762
440	0.50472	0.82683	0.92766	0.83739	0.88929
441	0.51255	0.62275	0.62886	0.65421	0.68366
522	0.51255	0.26128	0.26384	0.19957	0.20855

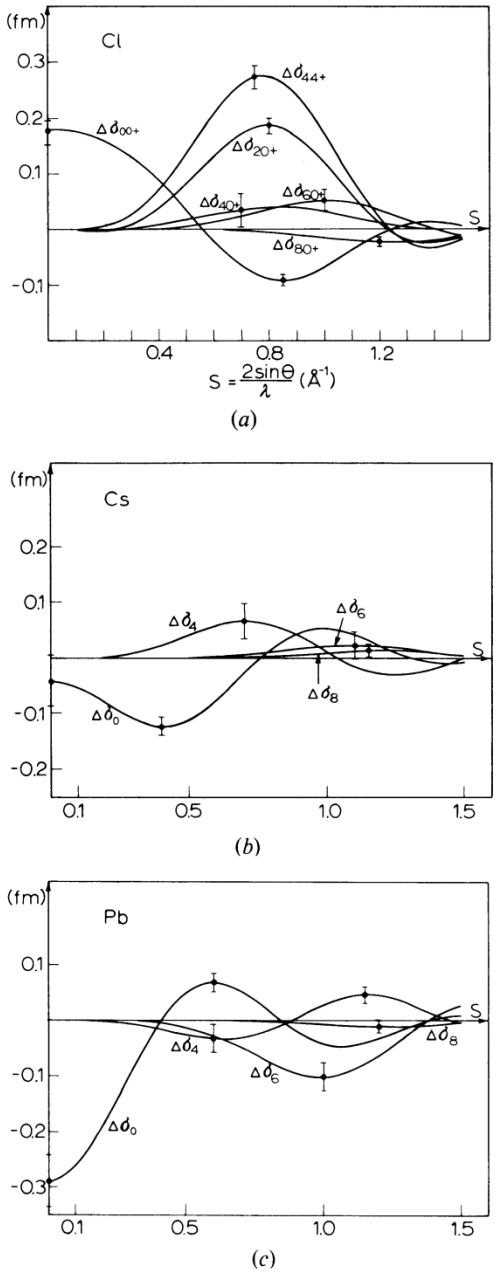

Fig. 2. (*a*) The radial scattering factors $\Delta\sigma_{lmp}(S)$ of Cl. (*b*), (*c*) The radial scattering factors $\Delta\sigma_{lu}$ of Cs and Pb, calculated by using $G_j^{\rm obs,1} - G_j^{\rm theor,1}$ as coefficients in the series (5).

model with the atoms vibrating harmonically around their ideal perovskite positions. The atomic site symmetries yield spherical temperature factors for the Pb and Cs atoms and an axial one for the Cl atom. The parameters are those obtained from the profile refinement (Table 1). The structure factors used in the analysis are compiled in Table 2.

The analysis is conducted in terms of the multipole components of the scattering factor $\sigma_n(S)$ in (5). The radii R_n of the spheres containing the nuclear distribution are chosen as half the distance between the Pb and Cl atoms, *i.e.* $R_{Cs} = R_{Cl} = R_{Pb} = 1{\cdot}4$ Å. The choice of the indices l,m,p and l,μ and the local coordinate axes, to which the multipole components have to be referred, conform to the point symmetries of the atoms in the way indicated by Kurki-Suonio (1977) and shown in Fig. 1. The radial scattering factors $\Delta\sigma_{lmp}$ from the application of equation (5) are shown in Fig. 2 with the error bars referring to the statistical errors in the experimental structure factors. It follows from the nature of the reference model that for Cs and Pb all nonspherical components ($l \neq 0$) and for Cl the components with $m \neq 0$ can be understood directly as σ_{lmp}.

4. Implications of the multipole analysis

The most striking feature in the results is the major 44+ component of the Cl distribution in Fig. 2(*a*). It indicates a significant deviation of the nuclear distribution from cylindrical symmetry with the angular dependence $\cos 4\varphi$ in the local coordinate system of Cl in Fig. 1. This means that the Cl atom in its distribution perpendicular to the Pb–Cl connecting line avoids the directions where the neighbouring Cs atoms are located.

The other large component 20+ of the Cl distribution indicates a deformation of the angular form $-\frac{1}{2}(\cos^2\theta - 1)$ from the harmonic model – the minus sign is due to the factor i^l in the Fourier Bessel transformation relating the radial scattering amplitudes to the radial densities (Kurki-Suonio, 1977). This, further, means that the Cl atoms are more concentrated on their local xy planes than is indicated by the harmonic model. Both components, 44+ and 20+, thus consistently seem to support a disorder of the Cl atoms into the four positions $\frac{1}{2},\pm u,0$; $\frac{1}{2},0,\pm u$ or alternatively corresponding highly anharmonic soft vibrations.

In the interpretation of the results the other components have minor significance. Particularly, there is little indication of any disordering or anharmonicity of the Cs and Pb distributions [see Fig. 2(*b*) and (*c*)]. The 6th order component of Pb seems significant but vanishing of the 4th order component shows that no simple interpretation exists.

The results do not give any clear indication of the dynamical model that should be used in their interpretation. Moreover, there is no clear hint on a distinction between the two extreme interpretations, disorder and anharmonic motion around the ideal positions. There has been some discussion of the possibility of disorder of the ions occurring in this compound. Therefore we make a more detailed study to find out whether our data allow such an interpretation. The disorder model to be used is obviously that with Cl in the positions $\frac{1}{2},\pm u,0$; $\frac{1}{2},0,\pm u$.

The scattering amplitude of the disordered Cl with axial thermal motion can be written in the form (Ahtee *et al.*, 1979)

$$\sigma(\mathbf{S}) = \exp\{-\tfrac{1}{4}S^2[\bar{B} + \Delta B y_{20+}(\theta_S,\varphi_S)]\}\, g_{Cl}[j_0(2\pi S r_{Cl}) + \sum_{l>0} i^l c_{lmp} j_l(2\pi S r_{Cl}) y_{lmp}(\theta_S,\varphi_S)], \quad (6)$$

where $\bar{B} = \frac{1}{3}(2B_{11} + B_{33})$ and $\Delta B = B_{33} - \bar{B}$ and

$$c_{lmp} = \frac{4\pi y_{lmp}([100])}{\int y_{lmp}^2 \,\mathrm{d}\Omega}, \quad (7)$$

giving $c_{20+} = -5/2$, $c_{40+} = 27/8$ and $c_{44+} = 315/64$. The disorder is responsible for the expansion in the latter square brackets in (6).

Let us first assume the thermal motion to be isotropic. In this case equation (6) gives directly the multipole expansion of $\sigma(\mathbf{S})$. Such a model would interpret the whole anisotropy of the Cl distribution in terms of the disorder parameter r_{Cl}, the displacement of the Cl atom. Qualitatively – as compared to the basic reference model – this has the advantage of giving a positive 44+ component. Since the disorder is in the local xy plane, B_{33} will keep approximately its initial value 1·99 Å^2, which, thus, gives the value of $\bar{B}$ for the isotropic case. The order of magnitude of r_{Cl} can be obtained by minimizing

$$\int |\sigma_G - \sigma|^2 \,\mathrm{d}^3S, \quad (8)$$

where σ_G is the anisotropic Gaussian smearing function of the reference model and σ the superposition of four disordered isotropic Gaussians. This yields $r_{Cl} = 0{\cdot}361$ Å.

The radial scattering amplitudes of the model 1 for the components lmp = 20+, 40+, 44+, in equation (6) are drawn in Fig. 3 together with the corresponding experimental results. Fig. 3 shows clearly that this simple model fails to describe the experimental nuclear distribution. To explain the components 20+ and 40+ a much larger disorder parameter r_{Cl} would be desirable. This, however, would yield a still larger component 44+.

An obvious way to improve the model is to apply an anisotropic temperature factor, where $\Delta B \neq 0$ in (6). To obtain the multipole components of the smearing

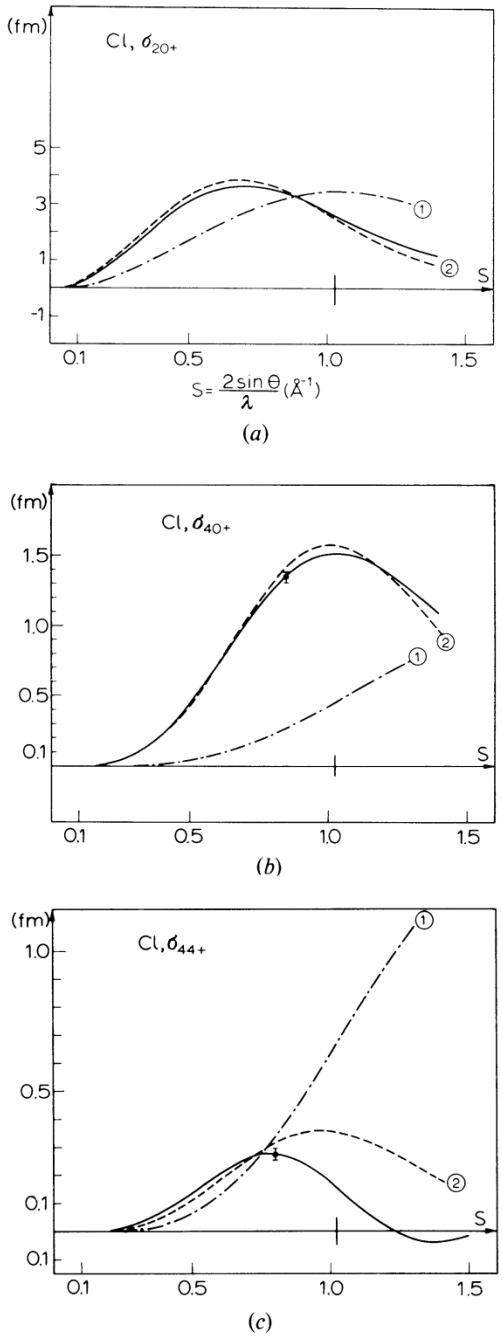

Fig. 3. (*a*) The radial scattering factor σ_{20+} of Cl, —— experimental. The experimental σ_{Imp} are obtained by adding the $\Delta\sigma_{Imp}$ of Fig. 2(*a*) to the components of the reference model; – – – – model 1, where $r_{Cl} = 0{\cdot}361$ Å, $\bar{B} = 1{\cdot}99$ Å^2; ------ model 2, where $r_{Cl} = 0{\cdot}450$ Å, $B_{11,Cl} = 8{\cdot}0$ Å^2, $B_{33,Cl} = 1{\cdot}99$ Å^2. (*b*) σ_{40+} of Cl. (*c*) σ_{44+} of Cl. The experimental cut-off value of 2 sin θ/λ occurs at 1·026 Å^{-1}.

function the expression (6) as a whole must be re-expanded.

It is again reasonable to have B_{33} fixed. A systematic variation of ΔB and r_{Cl} and comparison of the multipole components 20+, 40+, 44+ with the corresponding experimental results leads to the model 2 with $B_{11} = 8{\cdot}0$ Å^2, $B_{33} = 1{\cdot}99$ Å^2 and $r_{Cl} = 0{\cdot}450$ Å, which seems to give a reasonable fit within the observed region extending up to 2 sin $\theta/\lambda = 1{\cdot}026$ Å^{-1}. It should be noted (Kurki-Suonio, 1968) that the cut-off of the data necessarily suppresses the experimental curves at the sin θ/λ values close and above the experimental cut-off so that even in the case of 44+ the fit is reasonable.

In order to reach the best possible fit we refined the disordered model further with the aid of the Rietveld program starting from the values obtained for B_{11}, B_{33} and r_{Cl}. In the space group $Pm3m$ the disordered Cl atoms are in positions 12(*h*): $\frac{1}{2},x,0$ with the point symmetry *mm*. This gives the restrictions $B_{11} \neq B_{22} \neq B_{33}$, $B_{12} = B_{13} = B_{23} = 0$ for the anisotropic temperature factors. The resulting parameters are collected in Table 1, and the structure factors in Table 2.

5. Discussion and conclusions

The behaviour of the radial scattering amplitudes of the Cs and Pb atoms in Fig. 2(*b*) and (*c*) does not indicate any disordering or anharmonicity in the nuclear distributions of the Cs and Pb atoms. Instead, the significant 44+ component of the Cl atom indicates bulging of the smearing function in the local **x**– and **y**– directions. The 40+ and 20+ components indicate a stronger concentration of the smearing function in the local *xy* plane than in any harmonic model. The possible systematic experimental errors affect mainly the spherical components and can have only a minor effect on these types of conclusions concerning the nonsphericity of one particular kind of atom in the unit cell.

The refinement of the anisotropic disordered model shows a decrease of the reliability index R from the value 3·9% for the anisotropic perovskite structure to 2·4%. It is possible to interpret the results in terms of a disordered model, where the Cl atoms are at four equivalent positions $\frac{1}{2},\pm u,0$; $\frac{1}{2},0,\pm u$. Each Cl atom vibrates anisotropically around these positions so that the Cl atom has the same r.m.s. amplitude as Pb along the Pb–Cl connecting line. Furthermore, the Cl atom has almost the same r.m.s. amplitude as the Cs atom in the plane perpendicular to the line Pb–Cl.

It is, however, obvious from the behaviour of the multipole components of the models in Fig. 3 that our data are not sufficient to distinguish between disordering and anharmonicity of Cl. A possible multipeaking of the distribution is beyond the resolution and would require extension of the data to larger sin θ/λ.

A very recent work of Hutton, Nelmes, Meyer & Eiriksson (1979) presents a more extensive data set and their analysis. Our results on the behaviour of the smearing functions are in good agreement with their conclusions.

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