(Hirshfeld, 1976). Neutron data are highly desirable when hydrogen atoms are present, however; but note Stevens & Hope (1975).

(iv) Series-termination effects do not arise in a refinement approach.

(v) There is no 'noise' as such in the resulting deformation maps.

(vi) A deformation refinement should give an essentially correct scale factor.

(vii) An estimate of the error in the refined deformation density is readily obtainable.

An $X - N$ map, at least for a centrosymmetric structure, can nevertheless serve the useful purpose of representing the difference density unbiased by functions chosen to describe the deformation. It can thus be used to assess appropriate constraints for a subsequent deformation model refinement.

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SHORT COMMUNICATIONS

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Convergence of Brillouin zone summations.

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A simple method to overcome convergence problems in Brillouin zone summations of lattice dynamical properties is proposed, which makes use of evenly spread sample points and gives a special treatment to points close to the Brillouin zone origin.

Calculation of **T**, **L** and **S** tensors and thermal diffuse scattering involves integration over the Brillouin zone (BZ), or part of it, of functions which are quadratic in the vibration amplitudes **u**. For the acoustic modes σ with small wave vector **k**, the **u** values vary according to

$$\mathbf{u}(\sigma\mathbf{k}) = D(\sigma\hat{\mathbf{k}})/\mathbf{k}, \tag{1}$$

where $D(\sigma\hat{\mathbf{k}})$ is a function smoothly varying with $\hat{\mathbf{k}}$, and $\hat{\mathbf{k}}$ is a unit vector in the direction of **k**. Because

$$\lim_{\mathbf{k}\to 0} u^2(\sigma\mathbf{k}) = \infty \tag{2}$$

difficulties arise if the integration is to be done numerically since the contribution $I(v_0)$ of the volume element v_0 around $\mathbf{k} = 0$ cannot be obtained as $u^2(\sigma,\mathbf{k} = 0)\,v_0$. An estimate of this contribution can be obtained by analytical integration of (1). For a cone around **k** with opening angle $\mathrm{d}\psi$ and its apex coinciding with $\mathbf{k} = 0$ the integrated value is given by

$$I(\mathbf{k}) = D(\sigma\hat{\mathbf{k}})\,k_{\max}\,\mathrm{d}\psi, \tag{3}$$

where $k_{\max}$ is the height of the cone. From this it can be seen that for numerical integrations extremely dense sampling around $\mathbf{k} = 0$ is required to make $I(v_0)$ negligibly small with respect to the contributions of the remaining volume elements, since $I(v_0)$ does not approach zero with v_0 (or $k^3_{\max}$) but with $k_{\max}$. Filippini, Gramaccioli, Simonetta & Suffritti (1976) proposed a method to overcome the convergence problem which is based on a non-isometric sampling grid with dense sampling around $\mathbf{k} = 0$. We have tested their method by calculating the integral of a simple k^{-2} function, but have not achieved the improvement in convergence claimed in their paper. Moreover, sampling methods which make use of unevenly distributed grid points require more programming effort and can become quite cumbersome in, for instance, the double BZ summations occurring in the expressions for the second-order thermal diffuse scattering (Kroon & Vos, 1978*a*).

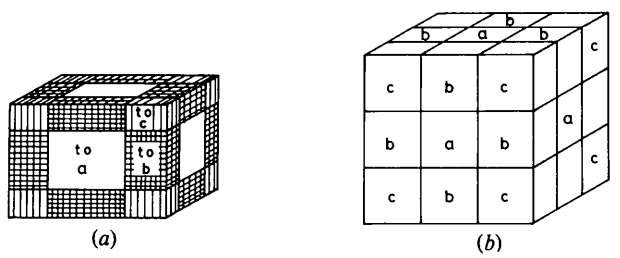
Since the convergence problem is caused by the behaviour of the acoustic lattice vibrations close to $\mathbf{k} = 0$, and the shape

of the functions to be integrated in that region is mainly determined by the k^{-2} term, it is possible to use an integration method in which the contribution of the element around the origin is estimated in the special way described below. The sampling points are evenly distributed throughout the BZ, the division being made along each of the reciprocal axes $\mathbf{a}^*(i)$. The contribution of v_0 is estimated from the nearest 26 surrounding elements. The v_0 element is divided into pyramids, each of which is directed to one of the surrounding elements as shown in Fig. 1(*a*), and the functional form (1) is assumed. Then the contribution $I(v_0)$ in terms of those of the surrounding elements (of which there are three types: *a*, *b* and *c*; Fig. 1*b*) can be derived as

$$I(v_0) = 0{\cdot}5 \sum_a I(v_a) + 0{\cdot}5 \sum_b I(v_b) + 0{\cdot}375 \sum_c I(v_c). \quad (4)$$

The method was tested by numerical integration of the function k^{-2} with a spherical volume as BZ. If the number of volume elements is taken to be sufficiently large, effects on the surface of the sphere can be neglected. The result of the integration is systematically too low, however, because of the inverse quadratic form of the function, the contribution of the volume elements with small $\mathbf{k}$ is systematically too small. This effect is accounted for by multiplying $I(v_0)$ as obtained from (4) by an empirical factor η. Calculations with various choices of the mesh sizes of the sampling grid and different axial directions showed η to be independent of these choices to a good approximation. From the values 1·29 and 1·33 obtained for reasonable grids, the value 1·31 was adopted. The practical implementation of this method merely consists of multiplying the vibration amplitudes $\mathbf{u}(\sigma\mathbf{k})$ for $\sigma = 1, 2, 3$ for the *a*- and *b*-type volume elements by $(1 + 0{\cdot}5\eta)^{1/2}$ and for the *c*-type elements by $(1 + 0{\cdot}375\eta)^{1/2}$.

Results of the calculation of **T** and **L** tensors with this improved method are shown in Fig. 2 (continuous lines). As expected, addition of the $I(v_0)v_0$ contribution has no effect on the **L** tensors, while the convergence for the **T** tensors improves drastically. As can be seen from the figure the calculated T values with finite grid sizes are slightly too small compared to the values extrapolated to $n = \infty$. For the grid size used in Kroon & Vos (1978*a*) the underestimation in **T** amounts to 0·5–3·5% with the improved method, while no significant errors remain in the **L** tensor.



(*a*) (*b*)

Fig. 1. (*a*) Division of the v_0 element into pyramids. The figure shows the bases of the pyramids on the surface of the v_0 element, each of them pointing to one of the surrounding volume elements, of which there are three types, shown in (*b*).

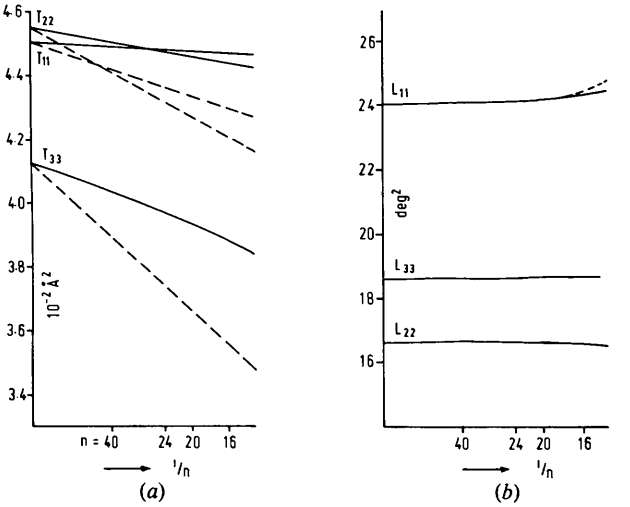


Fig. 2. Convergence of Brillouin zone summations for **T** and **L** tensors of naphthalene at 300 K. For formulae and interaction functions used, see Kroon & Vos (1978*a*). The curves show the dependence of the diagonal elements of **T** and **L** on the grid size for the numerical integration. n is the number of intervals along each reciprocal axis. ---- conventional isometric sampling. —— isometric sampling with estimation of the contribution of the $\mathbf{k} = 0$ element.

Apart from the calculation of **T** and **L** tensors, the above method has been applied in a comparative study of the effect of various approximations used in the calculation of thermal diffuse scattering corrections for X-ray diffraction intensities (Kroon & Vos, 1978*b*).

The computations were performed at the Computing Centre of the University of Groningen.

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