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As some of their lattice properties are estimated in the harmonic approximation, the amplitudes of the molecular motions for naphthalene and anthracene crystals have been calculated. Comparison between the results obtained either by a full dynamical calculation (i.e. tensors L and T) or by the simplified Cruickshank's theory with the values deduced from X-ray experiments is presented. In addition, the temperature dependence of molecular motions in naphthalene crystal is given in a wide range (from 77 K up to sublimation temperature).

1 INTRODUCTION

In the last few years, interest in the lattice vibrations of molecular solids has been centered around the elucidation of intermolecular potential functions. If a pair potential, as usual, is assumed, it can be tested by calculating optical external frequencies by application of lattice dynamics.

In molecular crystals, internal frequencies are generally higher than the lattice frequencies: therefore the two classes of motion are mostly separable. In this approximation of rigid bodies, it is possible to study the lattice vibrations separately. The motions of the molecules can be divided into two types: translational displacements of the centers of mass and librational displacements.

For the sake of simplicity, we only consider the special case when translational motions are separable from angular motions. Such a separation is valid only for centrosymmetric crystals at $\mathbf{k} = 0$. Pawley[1] has shown how both optical and acoustical branches acquire mixed character as the wave vector increases.

The lattice dynamics of translational motions has been formulated for a long time.[2] As pointed out by Schnepp,[3] for the angular motions, the classical treatment is valid only if the amplitudes of librations are small enough. This procedure amounts to the so called "harmonic approximation." For the calculations of lattice dynamics, this hypothesis is of great importance; thus it is possible to calculate several quantities: phonon dispersion curves, one-phonon density of states, elastic constants, velocities of acoustical waves, thermodynamic functions. All of them can be related to experimental data. In a recent paper[4] we have given a method to determine the dynamical matrix eigenvectors, in which one of the basic approximations is the harmonic approximation. Application has been done for naphthalene and anthracene crystals, therefore it is relevant to investigate a posteriori the validity of this hypothesis for both organic solids.

2 CALCULATIONS OF MOLECULAR MOTIONS IN LATTICES

In an interesting paper, Cruickshank[5] has given a simple method to determine the lattice vibrations amplitudes: for crystal of orthorhombic or lower symmetry having two molecules in the unit cell, the mean-square amplitude $\langle u_i^2 \rangle$ of translation vibration of the center of mass of a molecule along the i-axis is given by:

$$\langle u_i^2 \rangle = \tfrac{1}{2}\left\{\frac{3h^2\,T}{4\pi^2 mk\,\theta_M^2}\left(\phi(x) + \frac{x}{4}\right) + \frac{h}{8\pi^2 m\,\nu_i}\coth\tfrac{1}{2}\left(\frac{h\nu_i}{kT}\right)\right\} \tag{1}$$

with

$$\phi(x) = \frac{1}{x}\int_0^x \frac{\xi\,d\xi}{e^{\xi}-1}\,; \quad x = \frac{\theta_M}{T} \tag{2}$$

θ_M = Debye temperature

The first term gives the contribution from the acoustic branch and the second the contribution from the optical branch (ν_i is the optical frequency).

Similarly, the mean square amplitude $\langle \theta_j^2 \rangle$ of libration around a j-axis is:

$$\langle \theta_j^2 \rangle = \frac{h}{8\pi^2 I_j}\left\{\frac{1}{2\nu_1}\coth\left(\frac{h\nu_1}{2kT}\right) + \frac{1}{2\nu_2}\coth\left(\frac{h\nu_2}{2kT}\right)\right\} \tag{3}$$

I_j is the involved inertia moment; ν_1 and ν_2 are the $\mathbf{k} = 0$ frequencies for the symmetric and the antisymmetric librational modes.

It must be pointed out that for the relations (1) and (3), the dispersion of the optical modes is ignored.

Although these relations constitute a rather rough approximation, we will see that the results are in good agreement with those given by more sophisticated methods.

A correct calculation of the molecular motions in a crystal must take into account the distribution of frequencies in each of the external branches. Cruickshank[6] has shown that the anisotropic temperature factors obtained from Fourier least squares structure refinements can be described in terms of two tensors T and L. T gives the mean-square translational displacement and L the mean-square librational displacement from equilibrium.

Following Pawley,[1] we have for such tensors:

$$T_{ij} = \sum_{1\,2N\ \text{modes}} \frac{\xi_i \xi_j \varepsilon(\omega)}{Nm\omega^2} \tag{4}$$

$$L_{kl} = \sum_{1\,2N\ \text{modes}} \frac{\xi_k \xi_l \varepsilon(\omega)}{N\sqrt{I_k}\sqrt{I_l}\omega^2} \tag{5}$$

(see Ref. 1 for further details about the notation) where ξ_i, ξ_j are the real and imaginary coefficients of translational components of the eigenvectors, ξ_k and ξ_l are the same coefficients for librational components; $\varepsilon(\omega)$ is given by:

$$\varepsilon(\omega) = \hbar\omega\left\{\left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right]^{-1} + \tfrac{1}{2}\right\} \tag{6}$$

The summation is extended to the N points in the Brillouin zone. Such tensors can be obtained from the results of crystal structure analysis from X-ray or Neutron-diffraction.

3 APPLICATION TO NAPHTHALENE AND ANTHRACENE CRYSTALS

Both naphthalene and anthracene crystals belong to the monoclinic system of space group C_{2h}^5 with two molecules in the unit cell on C_i sites.[7,8] For the former, unit cell parameters were known at room temperature for a long time[7]; more recently, thermal expansion coefficients have been determined as functions of temperature[9]. From these new data we have calculated the crystal parameters in the range 80–350 K[10]; for each selected temperature, the molecular orientation in the unit cell is obtained by the minimization of the crystal potential energy following the method previously given by Taddei *et al*[11]. For anthracene crystal, the crystallographic structures have been determined only at 95 K and at room temperature[8]. Thus, we have already calculated the lattice dynamics of these two crystals at selected temperatures[12]

and shown that the Williams–IV potential[13] leads to calculated external frequencies in good agreement with the experimental data. Recently, we have published the eigenvectors corresponding to these external frequencies and shown that they are roughly fitted by those determined by the lattice modes intensities.[4] All of these calculations are correct only if the harmonic approximation is valid. Already, Pawley calculated the Debye–Waller factors for naphthalene and anthracene crystals but at room temperature only.[1] With relations (4) and (5), we first have computed the L and T tensors for both crystals at room temperature; the results of the calculations are the following:

$$T = \begin{vmatrix} 5.43 & -0.02 & 0.13 \\ & 4.20 & 0.70 \\ & & 4.10 \end{vmatrix} 10^{-2}\ \text{Å}^2 \qquad L = \begin{vmatrix} 28.0 & 1.80 & 0.60 \\ & 17.20 & 1.41 \\ & & 21.60 \end{vmatrix} \text{deg}^2$$

for naphthalene (296 K), and

$$T = \begin{vmatrix} 5.31 & -0.01 & 0.04 \\ & 3.16 & 0.82 \\ & & 3.39 \end{vmatrix} 10^{-2}\ \text{Å}^2 \qquad L = \begin{vmatrix} 18.85 & 0.68 & 2.74 \\ & 6.84 & 0.24 \\ & & 11.22 \end{vmatrix} \text{deg}^2$$

for anthracene (290 K).

These values must be compared with Pawley's lattice dynamical calculation of the T and L tensors for the same molecules (at 300 K):[1]

$$T = \begin{vmatrix} 4.14 & 0.08 & -0.05 \\ & 4.14 & -0.18 \\ & & 3.44 \end{vmatrix} 10^{-2}\ \text{Å}^2 \qquad L = \begin{vmatrix} 21.89 & 2.57 & 0.61 \\ & 15.67 & 2.47 \\ & & 17.22 \end{vmatrix} \text{deg}^2$$

for naphthalene, and

$$T = \begin{vmatrix} 4.19 & 0.10 & -0.16 \\ & 3.25 & 0.03 \\ & & 2.72 \end{vmatrix} 10^{-2}\ \text{Å}^2 \qquad L = \begin{vmatrix} 15.09 & 1.08 & 2.78 \\ & 5.98 & 0.49 \\ & & 9.01 \end{vmatrix} \text{deg}^2$$

for anthracene.

Although our lattice dynamical calculations[12] and those of Pawley lead to eigenvalues (related to the external frequencies), somewhat different, it is worth noting that the two sets of results are quite similar; for the tensors T, we obtain:

(i) diagonal elements slightly higher than Pawley,[1]

(ii) off-diagonal elements quite negligible;

for the tensors L, we observe:

(i) diagonal elements slightly higher than Pawley,[1]

(ii) some of the off-diagonal elements are significant: L_{12} for naphthalene and L_{13} for anthracene.

The similar tensors given in the literature are not directly deduced from experimental data and their numerical values depend significantly on the method of calculation. For example, from the same experimental data,[14] Pawley[1] and Cruickshank,[14] respectively, have deduced two sets of tensors for anthracene at 300 K:

$$T = \begin{vmatrix} 4.35 & 0.05 & -0.02 \\ & 2.98 & 0.02 \\ & & 2.33 \end{vmatrix} 10^{-2}\,\text{Å}^2 \text{ and } T = \begin{vmatrix} 3.87 & -0.12 & 0.01 \\ & 2.70 & 0.06 \\ & & 2.66 \end{vmatrix} 10^{-2}\,\text{Å}^2$$

$$L = \begin{vmatrix} 20.7 & 2.4 & 1.7 \\ & 6.9 & -0.7 \\ & & 10.5 \end{vmatrix} \text{deg}^2 \quad \text{and} \quad L = \begin{vmatrix} 14.56 & 1.57 & 0.87 \\ & 5.03 & -0.57 \\ & & 9.64 \end{vmatrix} \text{deg}^2$$

Moreover the standard deviation σ is very important; Cruickshank gives:

$$\sigma(T) = \begin{vmatrix} 0.12 & 0.11 & 0.12 \\ & 0.16 & 0.17 \\ & & 0.29 \end{vmatrix} 10^{-2}\,\text{Å}^2 \quad \sigma(L) = \begin{vmatrix} 5.45 & 0.75 & 1.51 \\ & 0.77 & 0.66 \\ & & 0.66 \end{vmatrix} \text{deg}^2$$

For naphthalene crystal, the values have been deduced at 290 K:[15]

$$T = \begin{vmatrix} 5.01 & -0.3 & 0.10 \\ & 4.0 & -0.5 \\ & & 3.44 \end{vmatrix} 10^{-2}\,\text{Å}^2 \quad \sigma(T) = \begin{vmatrix} 0.13 & 0.13 & 0.15 \\ & 0.18 & 0.18 \\ & & 0.36 \end{vmatrix} 10^{-2}\,\text{Å}^2$$

$$L = \begin{vmatrix} 19.5 & 2.25 & 2.56 \\ & 13.95 & 0.76 \\ & & 17.7 \end{vmatrix} \text{deg}^2 \qquad \sigma(L) = \begin{vmatrix} 6.6 & 1.34 & 2.43 \\ & 2.0 & 1.44 \\ & & 1.4 \end{vmatrix} \text{deg}^2$$

Owing to the magnitude of the standard deviation:

(i) the off-diagonal elements can be ignored

(ii) the precision on the elements of the trace is very rough.

The L and T tensors obtained by lattice dynamical calculation are in relatively good agreement with the above "experimental" tensors taking account of the standard deviation. When the calculated frequencies fit very well the spectroscopic data, some authors[16] feel that calculated L and T tensors are more valid than the results obtained from crystallographic data.

In Table I, r.m.s. amplitudes of librational motions for naphthalene and anthracene at room temperature are compared:

(i) column (a) gives the diagonal elements of the L tensors obtained by a full lattice calculations

(ii) column (b) refers to values given by the Cruickshank's formula in which $\mathbf{k} = 0$ experimental Raman frequencies are used.

(iii) in column (c) the Pawley's dynamical calculations are recalled.[1]

(iv) in the other columns, the diagonal elements of the L tensors deduced from X-ray patterns are listed.

The application of Cruickshank's theory leads to values lower than those obtained from the complete calculation for the entire Brillouin zone except for the librational motion around the W-axis. The reason is very clear from Pawley:[1] the two higher frequency optical branches (roughly describable as the U-axis librations) drop significantly in frequency as the wave vector increases, so that the weighted average frequency is lower than either of the two Raman frequencies. Thus, the high dispersion of these modes is confirmed; on the contrary the agreement between the values related to W-axis librations indicates that the corresponding branches have small dispersion as Pawley predicted[1] and that we have confirmed.[12]

Moreover these methods, based on the spectroscopic data, make it possible to easily derive the variation of the molecular motions with temperature; for naphthalene, lattice dynamical calculations have been performed at selected temperatures in the range 80–350 K and the L and T tensors estimated for the same temperatures. For clarity, we only give the roots of the L-diagonal ele-

TABLE 1

R.M.S Amplitudes of molecular motions

	Naphthalene (296 K)				Anthracene (290 K)					
$\langle\theta_j^2\rangle^{1/2}$ deg; $\langle u_i^2\rangle^{1/2}$ Å	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(e)	(f)	(g)
$\langle\theta_u^2\rangle^{1/2}$	5.29	3.46	4.68	4.42 ± 0.8	4.35	2.55	3.89	4.55 ± 1.2	3.60	3.16
$\langle\theta_v^2\rangle^{1/2}$	4.15	3.24	3.96	3.74 ± 0.3	2.62	2.10	2.44	2.63 ± 0.5	2.70	1.82
$\langle\theta_w^2\rangle^{1/2}$	4.65	4.10	4.15	4.21 ± 0.2	3.35	2.97	3.00	3.24 ± 0.4	3.10	2.80
$\langle u_u^2\rangle^{1/2}$	0.23	—*	0.20	0.23 ± 0.02	0.23	—*	0.20	0.21 ± 0.03	0.22	0.22
$\langle u_v^2\rangle^{1/2}$	0.20	—	0.20	0.20 ± 0.04	0.18	—	0.18	0.18 ± 0.04	0.17	0.20
$\langle u_w^2\rangle^{1/2}$	0.20	—	0.19	0.19 ± 0.09	0.19	—	0.17	0.16 ± 0.05	0.16	0.20

* R.M.S. amplitudes of translational motions have not been calculated: Cruickshank's formula gives a very rough approximation for acoustical modes; furthermore all of the optical translation frequencies are not well known.

(a) Trace elements of the dynamical tensors L and T.

(b) Values deduced from Cruickshank's formula (in which Raman experimental frequencies are used).[4]

(c) Trace elements of the dynamical tensors L and T from Pawley.[1]

(d)(e)(f)(g) Trace elements of the tensors L and T deduced from X-ray experiments. (d) Ref.[15] (290 K); (e), (f), (g) Refs. [14,8,16] (300 K).

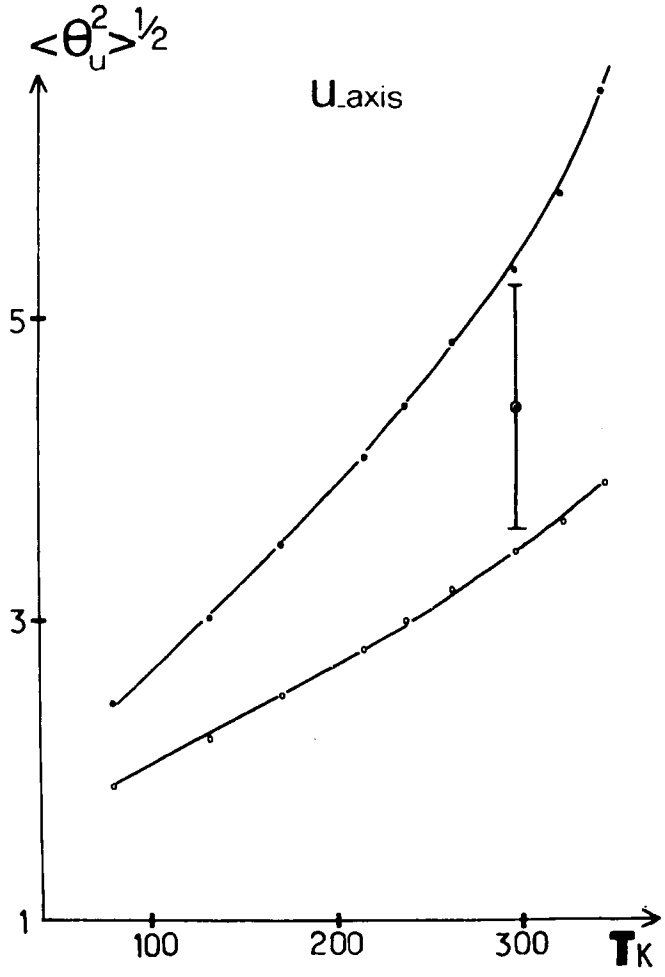

FIGURE 1 Temperature dependence on r.m.s. amplitudes of U-axis librational motions of naphthalene molecule in crystal. ● ● ●—diagonal element of lattice dynamical L tensor $\langle\theta_j^2\rangle_t^{1/2}$. ○ ○ ○—calculated values from Cruickshank's simplified theory using experimental Raman frequencies. ⊙—X-ray experimental data (Ref.[15]), estimated accuracy is indicated by a full vertical line.

ments versus temperature (they are labelled $\langle\theta_j^2\rangle_t^{1/2}$ (t means tensor); in Figures 1, 2, 3, these data are compared to r.m.s. amplitudes of libration given by Cruickshank's theory. We observe some discrepancies between these two sets of values: the main reason is the following: the former set related to lattice dynamical calculation involves calculated external frequencies for all $\mathbf{k}$, and the other uses $\mathbf{k} = 0$ Raman experimental frequencies.

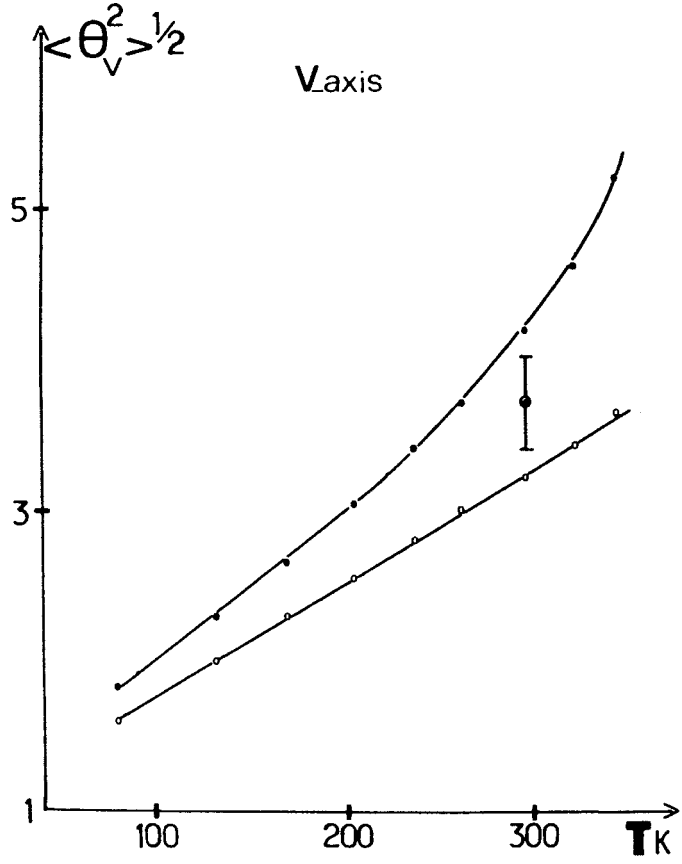

FIGURE 2 Temperature dependence on r.m.s. amplitudes of V-axis librational motions of naphthalene molecules in crystal (with the same notations as in Figure 1).

Nevertheless, the agreement between these two sets of values related to *W*-axis librations indicates the smallness of the dispersion of the corresponding optical branches, whatever the temperature.

Besides, for anthracene the same data are listed at room temperature (Table I). We also give the results of the calculations at 95 K (see Table II).

In the case of naphthalene crystal, $\langle\theta_j^2\rangle_t^{1/2}$ are about or smaller than 5° at room temperature; these amplitudes lead to estimates of a correction term in the kinetic energy of the order of 10%[3] (it is the order of magnitude of the anharmonicity). The librational motions around U-axis are less hindered, we also observe that the standard deviation given by X-ray pattern is the highest. Thus, it is not surprising that the corresponding calculated frequencies

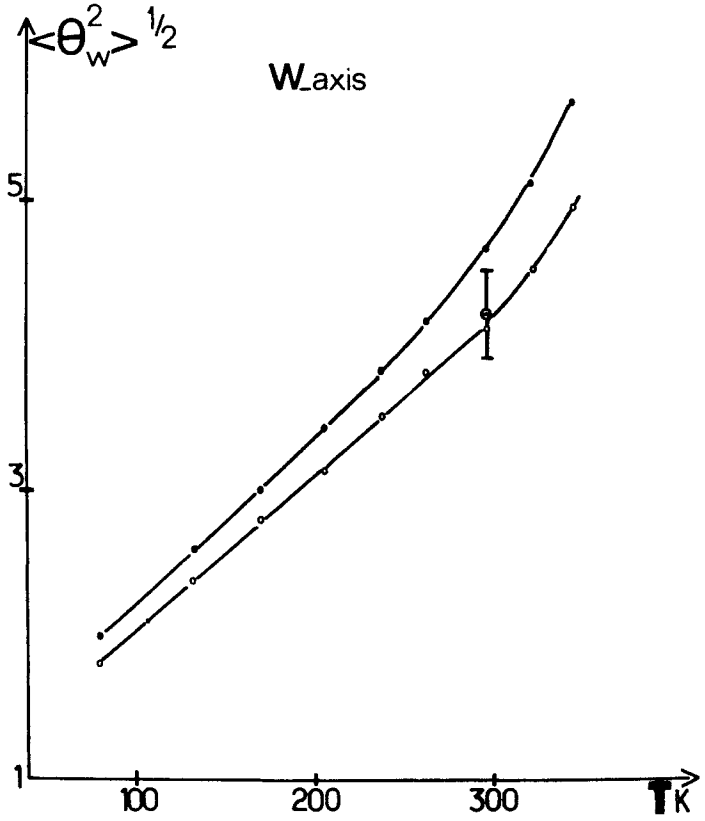

FIGURE 3 Temperature dependence on r.m.s. amplitudes of W-axis librational motions of naphthalene molecules in crystal (with the same notations as in Figure 1).

do not fit the Raman data well;[1,2] on the contrary, for the other modes, the calculated and experimental frequencies are in good agreement. From the shapes of the curves I, II, III, for very low temperatures a better agreement is evidently expected as we already have shown (at liquid nitrogen temperature $\langle\theta_j^2\rangle_t^{1/2} \leq 2°5$). As all the librational motions are more hindered for anthracene crystal, the dynamical calculations are a fortiori more available.

For naphthalene, just below the sublimation temperature (θ_s = 353 K), it is worth noting that the amplitudes of the librational motions are not very high: $\langle\theta_j^2\rangle_t^{1/2} \leq 7°$; so that even just below the sublimation temperature good agreement between calculated and experimental lattice frequencies is expected.[12]

TABLE II

Molecular motions in anthracene crystal

	$\langle\theta_j^2\rangle^{1/2}$ deg. $\langle u_i^2\rangle^{1/2}$ Å					
T (K)	$\langle\theta_u^2\rangle^{1/2}$	$\langle\theta_v^2\rangle^{1/2}$	$\langle\theta_w^2\rangle^{1/2}$	$\langle u_u^2\rangle^{1/2}$	$\langle u_v^2\rangle^{1/2}$	$\langle u_w^2\rangle^{1/2}$
290	4.35	2.62	3.35	0.23	0.18	0.19
	(2.55)	(2.10)	(2.97)	—*	—	—
95	2.18	1.24	1.59	0.11	0.08	0.08
	(1.50)	(1.10)	(1.42)	—	—	—

Upper values are the diagonal elements of dynamical tensors L or T.

Lower values (in brackets) are obtained by Cruickshank's simplified theory (Raman experimental frequencies are used).

* r.m.s. amplitudes of translational motions have not been calculated for the same reason as given in Table I.

4 CONCLUSION

For naphthalene and anthracene crystals, agreement between the X-ray scattering and the calculated values for molecular motions is quite satisfactory when we take into account the fairly large error involved in the X-ray estimates. Moreover, these X-ray values depend not only on the X-ray pattern, but also on the chosen method of calculation.

As a matter of fact, especially when the spectroscopic data are very accurate, as for naphthalene and anthracene, the r.m.s. amplitudes derived from the dynamical treatment are as reliable as those obtained from the crystallographic data.

Although the application of the simplified theory of Cruickshank gives values rather low, it leads to a correct order of magnitude for the amplitudes of the molecular motions; so it is very useful as a rapid criterion for an "a priori" harmonic treatment of lattice dynamics.

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