

where  $K_z$  is the  $z$  component of the unit scattering vector  $\hat{\mathbf{K}}$ . Varying the values of  $S_z$  and  $S_{\bar{x}}$  one finds (Corliss *et al.*, 1961) non-zero values such that the calculated intensities are in agreement with the observed. We conclude that the chromium spin arrangement is invariant under the spin translation group (331') where the rotations are about the  $z$  axis. The spins have both a component in the  $z$  direction and in the basal plane. This is the so-called 'umbrella' spin arrangement shown in Fig. 1. We note that the spin arrangement has not been uniquely determined since the orientation of the  $\bar{x}$  axis with respect to the crystal's hexagonal coordinate system, and consequently of the components of the spins in the basal plane, is unobtainable from the neutron diffraction data.

Relation (12) was also derived by Corliss *et al.* (1961), but only after *ad hoc* assumptions were made pertaining to the rotational symmetry of the spin arrangement. The advantage of applying the theory of spin translation groups in the analysis of neutron diffraction data is that information on the mutual orientation of spin can be obtained, without making any assumptions on the rotational symmetry of the spin arrangement, by using Tables 1 and 2. In fact, relation (12) was derived above by considering only the indices of the magnetic reflexions and the table of possible reflexions of spin translation groups.

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### Calculation of the T, L and S Tensors from Crystal Forces and *vice versa*

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It would be useful if the measured values of T, L and S could be used directly to give information about the intermolecular crystalline forces. This requires the assumption of an Einstein model for the molecular dynamics, where T, L and S are related through a smearing function to a molecular site potential function. It is shown that this potential function has no physical interpretation. Einstein-model calculations are compared with the physically justifiable Born-von Kármán calculations for four examples, sulphur, benzene, phenanthrene and pyrene, and very little regularity is apparent in the comparison of these results.

#### 1. Introduction

The average thermal motion of a rigid molecule in a crystal is correctly described by three tensors T, L and S which can be obtained from diffraction experiments. T and L describe respectively the mean-square trans-

lational and librational displacements, while S, first introduced by Schomaker & Trueblood (1968), takes account of the correlations between translation and libration. These tensors derive from averages over all the lattice modes of vibration whose number may be of the order of Avogadro's number. It is therefore unsafe

to try to interpret the values of **T**, **L** and **S** in terms of very simplified models – or so it would seem. It is the purpose of this paper however to investigate just how far a certain simple plausible assumption can retain its usefulness.

The diffraction effect of **T**, **L** and **S** can be thought of as resulting from a smearing function, which relates to a potential function for the molecule in real space. The only possible physical interpretation of this potential is that it is that potential which one molecule experiences by small displacements when all the neighbouring molecules are undisplaced. If this physical interpretation is realistic, then it is possible to calculate the potential uniquely once **T**, **L** and **S** have been measured. This would therefore be of great use in the study of intermolecular crystal forces, and it behoves us to investigate the validity of this assumption.

We are able to do this by using in two ways a realistic model for the lattice dynamics of crystals composed of rigid molecules. We follow closely the formulation of Pawley (1972*a*), but for more details of the lattice dynamics the reader is referred to Cochran & Pawley (1964), Pawley (1967) and Venkataraman & Sahni (1970).

## 2. The model

Imagine a crystal composed of rigid molecules. The requirement that the molecules be rigid presupposes that the internal modes of vibration of the molecules have frequencies sufficiently high that their contribution to the atomic displacements can be neglected. Although this assumption can be queried for all the examples considered later in this paper, this does not invalidate the main conclusion.

To calculate the dynamical behaviour of the molecules some form of intermolecular potential is required. This is furnished by assuming that the interaction between two molecules depends on all the vectors  $\mathbf{r}_{ij}^{EN}$  between the atoms (indexed *i*) of one molecule, *E*, and the atoms (indexed *j*) of the other molecule, *N*. If the energy associated with such a vector is

$$V_{ij}^{EN} = -\frac{A_k}{r^6} + B_k \exp(-\alpha_k r), \quad (1)$$

where  $r = |\mathbf{r}_{ij}^{EN}|$ , then the interaction energy for the pair of molecules is

$$V^{EN} = \sum_{ij} V_{ij}^{EN}. \quad (2)$$

The letter *N* is chosen to represent 'neighbour', and *E* is used for the 'basic molecule' as it is the letter used for the identity operation in group theory. The interaction energy between the basic molecule and all its neighbours is then  $2\Phi$ , where

$$\Phi = \frac{1}{2} \sum_N \sum_{ij} V_{ij}^{EN} \quad (3)$$

is the crystal potential energy per molecule. The factor of  $\frac{1}{2}$  appears because the energy in each bond is otherwise counted twice.

The finer details of the model are given in the references cited earlier, and as these are not essential for the presentation of our main argument, they are not reproduced here.

## 3. Use of the model

The potential function (3) is exactly that function mentioned in the Introduction: it is the potential that the molecule *E* experiences when none of the neighbours *N* are displaced. It is a simple eigenvalue problem to find how the *E* molecule will vibrate in such a potential, and the amplitudes which result may be expected to give **T**, **L** and **S**. Since this model ignores the effect of the movement of neighbours it is an Einstein model for the thermal motion of the crystal. It is well known that the shortcomings of such a model are avoided in a Born–von Kärman model, but the Einstein model, when appropriate, gains from its simplicity.

The values of **T**, **L** and **S** thus calculated are then compared with the results of a full Born–von Kärman lattice dynamical calculation. The total crystal potential (3) can be expanded in terms of small displacements of all the molecules. A dynamical matrix can then be set up for any phonon wave vector and the solution of the secular equation gives all the eigenvalues (frequencies) and eigenvectors for that wave vector. From this can be calculated the contribution to **T**, **L** and **S** for these modes (Pawley, 1968), and by selecting a sufficient number of wave vectors evenly distributed throughout the Brillouin zone these contributions can be summed to give tensors calculated to any required accuracy.

Before comparing the results of the two calculations it should be made clear and stressed that the validity of the result does not depend on whether or not the model is good. In all the examples used the model is fairly realistic but open to criticism. However we can state that given a potential function the Born–von Kärman calculation gives the correct result and the difference between this result and that from the Einstein model is a true measure of the approximation of the latter.

## 4. Results

Calculations have been done on four molecular solids: phenanthrene, pyrene, orthorhombic sulphur and benzene. The constants used for the potential function of equation (1) are given in Table 1.

Table 1. Constants used for the potential function of equation (1)

Atom pair <i>k</i>	$A_k$ kcal/(mole Å <sup>6</sup> )	$B_k$ kcal/mole	$\alpha_k$ Å <sup>-1</sup>
C···C	358	42000	3·58
C···H or D	154	42000	4·12
H or D···H or D	57	42000	4·86
S···S	1059	100000	3·50

Table 2 lists the information relevant to these four examples. The calculations of T, L and S from both models need to be done for a specific temperature, and so 300°K is chosen throughout (although benzene would be a liquid at this temperature). The results of the calculations are given in Table 3.

### 5. Conclusion

It is quite clear that there is no relationship between the results of the two model calculations close enough to be used quantitatively. Thus the measured values of T, L and S cannot be used to derive a potential

function of any physical significance, their only quantitative use is in comparison with the results of a full Brillouin-zone summation using some form of Born-von Kàrmàn model.

Close inspection of the results suggests that the Einstein-model calculation is being done with a potential which is too 'hard'. Table 2 contains the mean ratios between the diagonal elements from the two calculations for T and also for L, and as these vary over a wide range it is clear that a single 'softening' factor is inappropriate. That a softening factor is necessary results from the fact that the Einstein calculation assumes that the neighbouring molecules are held fixed.

Table 2. *Structural data*

	Sulphur	Benzene	Phenanthrene	Pyrene
Space group	<i>Fddd</i>	<i>Pbca</i>	<i>P2<sub>1</sub></i>	<i>P2<sub>1</sub>/a</i>
cell				
<i>a</i> (Å)	10.437	7.39	8.472	13.649
<i>b</i> (Å)	12.845	9.42	6.166	9.256
<i>c</i> (Å)	24.369	6.81	9.467	8.470
β (°)	—	—	98.01	100.28
Z	16*	4	2	4
Molecular site symmetry	2 <sub>z</sub>	$\bar{1}$	1	1
Modes used in B-vK calculation	1440	1728	720	1728
(Includes <i>q</i> and $-q$ )				
$\frac{\sum T_{ii}(B-vK)}{\sum T_{ii}(E)}$ †	2.1	2.1	2.6	3.4
$\frac{\sum L_{ii}(B-vK)}{\sum L_{ii}(E)}$ †	1.3	1.5	2.1	3.3

\* Z=4 for the primitive cell.

† Uses the results of Table 3.

Table 3. *Calculated values of T, L and S using the Einstein model (E) and the Born-von Kàrmàn model (B-vK) at a temperature of 300°K*

$T_{ij}$  are in  $10^2 \text{ Å}^2$ ,  $L_{ij}$  are in  $\text{deg}^2$ , and  $S_{ij}$  are in  $10^1 \text{ Å deg}$ .

	Sulphur		Benzene		Phenanthrene		Pyrene		From neutron data†
	E	B-vK	E	B-vK	E	B-vK	E	B-vK	
$T_{11}$	2.05	4.46	1.58	3.84	1.04	3.04	1.25	4.67	3.85
$T_{22}$	1.88	4.19	2.11	3.62	1.63	4.27	0.98	4.86	3.69
$T_{33}$	2.04	3.92	1.74	3.99	1.85	4.36	2.54	6.68	6.07
$T_{23}$	—	—	-0.19	-0.25	-0.10	0.50	0.22	0.35	0.47
$T_{31}$	—	—	-0.34	-0.56	0.22	0.59	0.45	0.64	0.86
$T_{12}$	-0.32	-0.89	-0.13	-0.51	0.32	0.56	0.46	0.72	0.82
$L_{11}$	21.5	29.4	18.9	28.2	11.5	22.1	7.3	25.0	18.9
$L_{22}$	15.3	20.1	33.1	48.5	6.7	10.4	9.2	31.1	18.0
$L_{33}$	20.0	26.3	20.0	28.3	11.2	29.3	8.5	26.1	19.1
$L_{23}$	—	—	-3.8	-6.4	1.5	2.0	1.3	11.0	2.7
$L_{31}$	—	—	-2.5	-6.7	-3.3	-5.8	1.8	1.4	2.9
$L_{12}$	-2.9	-4.5	-1.4	-2.6	-1.3	-2.8	-3.6	-13.2	-5.9
$S_{11}$	1.82	3.05	—	—	-1.28	-2.37	-0.25	0.07	*
$S_{22}$	-0.31	-0.15	—	—	1.11	1.75	0.23	-0.95	*
$S_{33}$	-0.38	-0.58	—	—	0.19	0.60	-0.08	-1.56	*
$S_{23}$	—	—	—	—	0.01	0.51	1.07	1.01	0.34
$S_{32}$	—	—	—	—	0.44	0.55	-0.28	-0.92	-0.44
$S_{31}$	—	—	—	—	1.03	1.66	-0.09	-0.87	0.16
$S_{13}$	—	—	—	—	0.09	0.28	-0.61	-0.80	-0.37
$S_{12}$	-0.48	-1.28	—	—	-0.62	-1.21	-0.24	0.16	0.12
$S_{21}$	-2.35	-2.61	—	—	0.52	1.34	0.30	-0.44	-0.13

\*  $S_{11} - S_{33} = -0.02$ ,  $S_{33} - S_{22} = 0.04$ ,  $S_{11} - S_{22} = 0.02$

† Values as in Pawley (1972b), but transformed to the molecular centre.

In reality the neighbours move and roughly these movements can be classified as 'in-phase' and 'out-of-phase'. For 'in-phase' movement the potential function is effectively softened, the mode frequencies are lowered and the amplitudes increased. This is not compensated fully by the 'out-of-phase' motions which correspond to raised frequencies and smaller amplitudes.

In the structures of benzene and sulphur the arrangement of neighbours is much more isotropic than in pyrene and phenanthrene. Comparison of the individual diagonal elements of **T** and **L** in the cases of benzene and sulphur shows no enormous discrepancy over and above a softening factor. However as the structure becomes increasingly anisotropic so the softening factor increases and detailed discrepancies appear.

The most striking discrepancy is in the value of  $T_{22}$  for pyrene. In this crystal pairs of molecules related by the centre of inversion lie on parallel planes distant 3.5 Å from each other, and they are almost perpendicular to the *b* axis. The close approach of so many atoms along this direction causes the potential to be very hard and the Einstein model gives a very small value,  $T_{22} = 0.0098 \text{ \AA}^2$ . The lattice-dynamical calculation yields a value of  $0.0486 \text{ \AA}^2$ , which is in good agreement with the experimental value of  $0.0369 \text{ \AA}^2$ . These experimental values come from the constrained refine-

ment of neutron diffraction data (see Pawley, 1972*b*), and show a satisfactory overall agreement with the Born-von Kármán calculation.

Thus it is possible to make qualitative arguments and conclusions using the diagonal elements of **T** and **L**. However no such argument can be used for the off-diagonal elements, including the elements of **S**. These are determined by the finer aspects of the molecular packing, and thus our understanding of intermolecular forces cannot be furthered by simple Einstein-model calculations. In many ways therefore our result is disappointing, but at least we learn to avoid making an assumption which is superficially plausible but which has no physical justification.

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## Multiple Scattering and Dynamical Effects in Diffuse Electron Scattering

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A many-beam dynamical theory for Bragg scattering effects in diffuse electron scattering is developed which takes multiple diffuse scattering into account. For non-absorbing crystals the theory is shown to include previous theories for Kikuchi lines and bands; with absorption, a weaker dependence on the anomalous absorption parameters than in previous theories is found. The variations in symmetrical Kikuchi-band contrast are discussed, and the thickness dependence of the angular range with excess contrast is explained. For typical higher-order systematic lines the theory predicts contrast variations similar to the ones found for the band, *i.e.* characteristic thickness-dependent disappearance angles and angle-dependent disappearance thicknesses for the line contrast. The low band contrast observed from very thick specimens is found to be due to the reduced anomalous absorption associated with the higher-order diffuse scattering contributions. Calculated Kikuchi-band contrast due to multiple thermal scattering in Si is given.

### Introduction

Bragg scattering effects in diffuse electron scattering, *i.e.* the Kikuchi lines and bands, have been discussed by various authors (Pfister, 1953; Kainuma, 1955; Takagi, 1958; Fujimoto & Kainuma, 1963; Gjønnes, 1966; Hall, 1970; Thomas & Humphreys, 1970; Ishida,

1971; Okamoto, Ichinokawa & Ohtsuki, 1971), and at present the absorption-independent diffraction effects observed from relatively thin crystals are well understood. In particular, qualitative explanations have been given for various effects observed in the narrow lines (Kambe, 1957; Gjønnes & Watanabe, 1966; Uyeda, 1968; Gjønnes & Høier, 1969; Lally,