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Thermal Vibrations in Cubic Crystals

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The relationships between the diffuse spots and non-radial streaks on 'diffuse' Laue photographs, and their significance in terms of the Waller–Jahn theory and the state of binding of the atoms, have been studied for cubic crystals, non-molecular and molecular in type.

The elastic behaviour of LiF and its effect on the diffuse scattering of X-rays has been compared with that of KCl and other alkali halides.

The results of the representation of diffuse spots in reciprocal space as anisotropic clouds around the reciprocal-lattice points, and the existence or non-existence of bridges of extra reflecting power from one reciprocal-lattice point to another, are studied for non-molecular cubic crystals and for the molecular cubic crystal $C_6N_4H_{12}$.

1. Introduction

Atoms vibrate about their mean lattice positions at ordinary temperatures with amplitudes that are comparable with X-ray wave-lengths. Using the values of the Debye characteristic temperature (as reported by Clusius, 1946), the root-mean-square amplitude of thermal vibrations in LiF can be determined (Lonsdale, 1948); it is found to be 0·124 Å at 80° K. and 0·174 Å at 273° K. Using the values of the amplitudes of vibrations of Li^+ and F^- in LiF as given by Havighurst (1926), the root-mean-square amplitude is 0·188 Å at 293° K. (see also Brindley, 1930). These atomic vibrations will cause a decrease in the intensity of the Bragg reflexions, but the total amount of scattering must remain the same. The difference in intensity appears in the form of extra reflexions on over-exposed Laue photographs. A diffuse pattern, composed of spots, streaks and sometimes diffuse patches superimposed on the Laue pattern, is frequently seen on well-exposed Laue photographs of stationary single crystals if the incident X-ray beam contains a strong characteristic component.

The extra reflexions on 'diffuse' Laue photographs of KCl have been studied by Lonsdale & Smith (1941). Jahn (1942) gave a simple manageable expression for the Faxen–Waller theory in the form

$$I \propto \frac{R^2}{r^2}\,\frac{c_{44}^2+\Sigma L^2\{c_{44}(c_{11}-c_{44})(m^2+n^2)+(c_{11}+c_{12})(c_{11}-c_{12}-2c_{44})m^2n^2\}-2\Sigma MNmn(c_{12}+c_{44})\{c_{44}+(c_{11}-c_{12}-2c_{44})l^2\}}{c_{11}c_{44}^2+c_{44}(c_{11}+c_{12})(c_{11}-c_{12}-2c_{44})\Sigma l^2m^2+(c_{11}+2c_{12}+c_{44})(c_{11}-c_{12}-2c_{44})^2l^2m^2n^2}\,.$$

I is the intensity of diffuse scattering at a distance r in the direction $[l, m, n]$ from a reciprocal-lattice point P, distant R from the origin of reciprocal space, the direction cosines of R being $[L, M, N]$; c_{11}, c_{12} and c_{44} are the elastic constants of a cubic crystal in the standard notation.

The isodiffusion contours plotted from Jahn's formula, using the elastic constants of KCl, gave good qualitative agreement with those obtained by observations on 'diffuse' Laue photographs of KCl (Lonsdale, 1942) and on monochromatic photographs taken by Guinier, though Jahn's formula is strictly applicable only in the close neighbourhood of the reciprocal-lattice points.

2. X-ray diffuse scattering by a single crystal of LiF

Although LiF has a NaCl-like structure, yet its elastic behaviour is different from that of KCl. It will be expected, therefore, that the diffuse X-ray scattering by LiF should be different from that of KCl. A complete set of 'diffuse' Laue photographs of a single crystal of LiF was taken using a crystal in the form of a small rectangular parallelepiped (1·75 × 0·92 × 0·95 mm.^{3}) with well defined faces, which showed no distortion. Both Laue and monochromatic photographs were obtained using a Victor X-ray tube, with copper target, operated at 32·5 kV. and 20 mA. An exposure time of 2 hr., with unfiltered copper radiation, was found satisfactory for the study of the diffuse spots on each of a complete set of cylindrical Laue photographs.

Shape and indexing of the diffuse spots

The characteristic shapes of the diffuse spots are shown on the accompanying photographs (Figs. 1 and 2) and are seen to be independent of those of the corresponding Laue spots. Any diffuse spot on a 'diffuse' Laue or monochromatic photograph can be quickly indexed by a simple comparison with the cylindrical rotation photograph. The position of the diffuse spots corresponds rather closely (but not necessarily exactly, especially when the atomic plane

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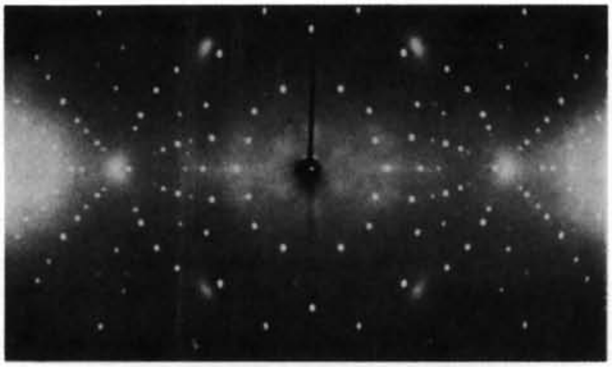

Fig. 1. LiF. Filtered Cu radiation along $[10\bar{1}].[010]$ vertical. Exposure 6 hr., 32·5 kV., 20 mA. Notice crescent shape of the diffuse spot $00\bar{4}$ (on equator), quite independently of the shape of the corresponding Laue spot. No non-radial streaks visible.

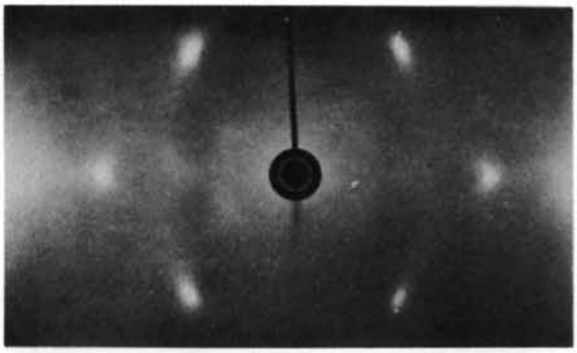

Fig. 2. LiF. Monochromatic Cu $K\alpha$ radiation along $[10\bar{1}].[010]$ vertical. Exposure 25 hr., 32·5 kV., 20 mA. Notice weak diffuse non-radial streak, its direction corresponding to the characteristic shape of the diffuse spot $00\bar{4}$.

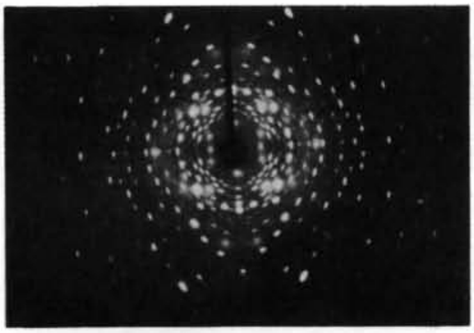

Fig. 3. $NaClO_3$. Filtered Mo radiation nearly along $[001].[010]$ vertical. Exposure 4 hr., 50 kV., 10 mA. Notice streak direction and shape of diffuse spots.

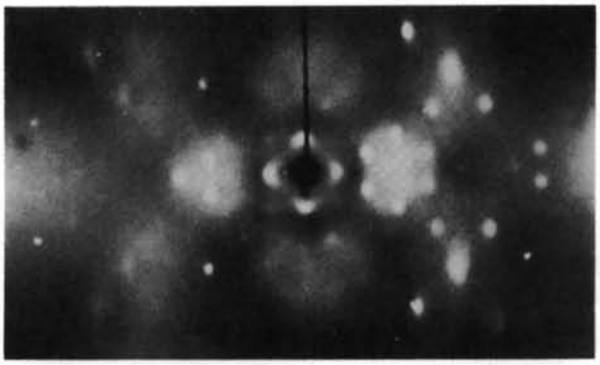

Fig. 4. Hexamine. Monochromatic Cu $K\alpha$ radiation 3·85° from $[001].[1\bar{1}0]$ vertical. Exposure 25 hr., 32·5 kV., 20 mA. In this particular orientation there is a correspondence between the shape of the diffuse spot 110 (equatorial, nearest to centre) and the streak $110 \rightarrow 1\bar{1}0$, but this does not prevent the vertical streak $200 \rightarrow 020$ from passing through the 110 diffuse spot.

Table 1. *Elastic constants*

(Unit: 10^{11} dyne cm.$^{-2}$)

		c_{11}	c_{12}	c_{44}	c_{11}/c_{44}	References
KCl	(1)	3·70	0·81	0·79	4·57	Schmid & Boas (1935)
	(2)	4·3	0·75	0·79	5·44	Ramachandran & Wooster (1951)
NaCl		4·97	1·27	1·27	3·91	Bhagavantam (1946)
LiF	(1)	12·00	4·41	6·40	1·875	Bergmann (1938)
	(2)	9·74±0·01	4·04±0·02	5·54±0·03	1·76	Huntington (1947)
	(3)	9·9	4·3	5·4	1·83	Hoerni & Wooster (1952)

is a long way from its Bragg reflecting position) to the position of the Bragg spots.

Representation of diffuse spots in reciprocal space

In Fig. 5(*a*) each diffuse spot is shown as an arc of the appropriate sphere of reflexion, allowance being made for the width of the corresponding Laue spots. Dotted parts of some arcs means that the ends of the diffuse spot along the central layer line cannot be measured with certainty owing to the interference of a Laue spot rather close to the diffuse spot.

Jahn contour

Bergmann (1938, p. 180) has determined the elastic constants of LiF by an optical method. Huntington (1947), by ultrasonic measurements on single crystals, determined the elastic constants for LiF and other alkali halides. Ramachandran & Wooster (1951) have determined the elastic constants of several cubic crystals from diffuse reflexion of X-rays. Using this method, but with photographic data for intensity measurements, Hoerni & Wooster (1952) have determined the elastic constants of LiF. All sets of measurements, however, give a much smaller value of the ratio c_{11}/c_{44} for LiF than for other alkali halides.

The general shapes of the equi-reflecting contours are not sensitive to variations in elastic constants of LiF of the order of those given by the three different methods, but they do show a marked difference between LiF and the other alkali halides examined. A good qualitative agreement is found between the shapes of equi-reflecting contours in Fig. 5(*a*) and those calculated (Fig. 5(*b*) using Bergmann's values) from Jahn's formula. Table 2 shows the dissimilarity in the elastic behaviour of KCl, NaCl and LiF, as predicted by Jahn's formula.

It is important to notice that although Jahn's formula may strictly be applied only in the close neighbourhood of the reciprocal-lattice points, since it takes into account only the long wavelengths in the acoustic branch, yet it not only does predict the precise shape of the diffuse spot but it also indicates the possibility of an extension of extra reflecting power right across from one reciprocal lattice point to another along certain specified directions which may differ for different substances.

Non-radial streaks

Non-radial streaks appeared on monochromatic photographs of LiF (pentaerythritol being used as the

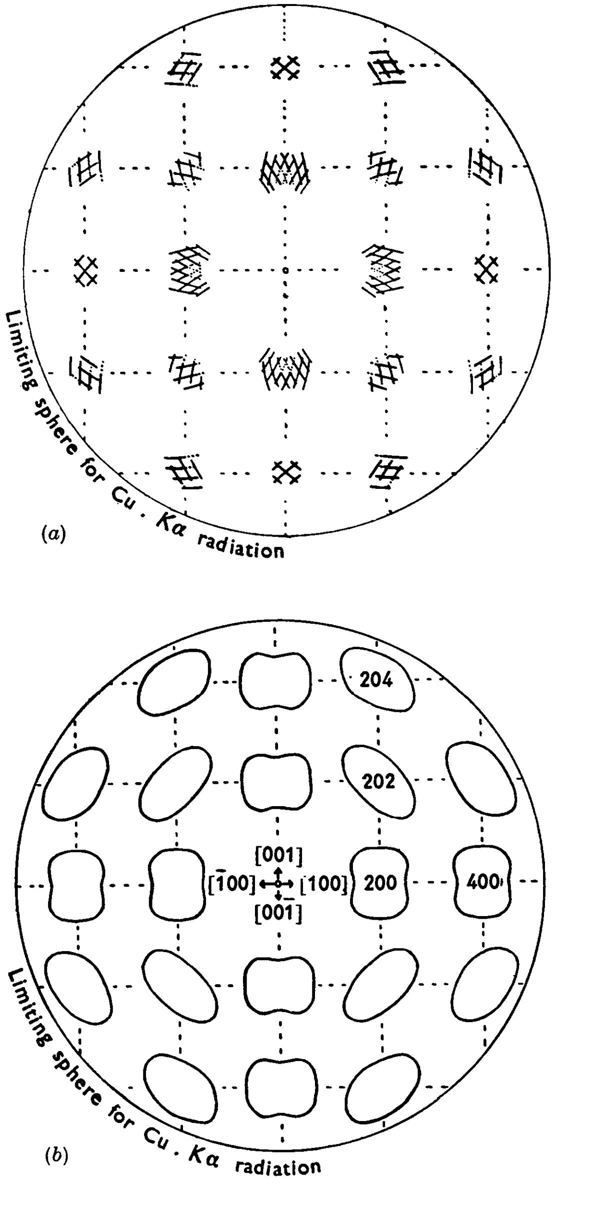

Fig. 5. (*a*) LiF. Cu $K\alpha$. Reciprocal net showing positions of diffuse spots on central layer line of Laue photographs taken with cube axis of crystal vertical. Notice concentration of extra reflecting power in the immediate neighbourhood of reciprocal-lattice points. No extension of extra reflecting power from one reciprocal-lattice point to another. Compare with representation for KCl (Lonsdale & Smith, 1941). (*b*) Equi-reflecting contours in the net $k = 0$. Notice relative shapes of the Jahn contours.

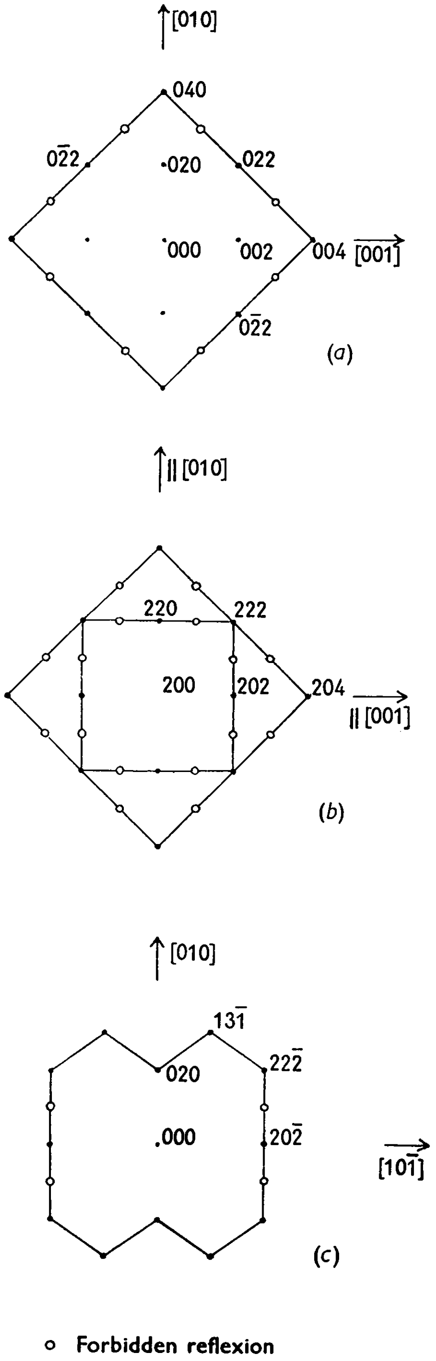

Fig. 6. (*a*) Formal representation of diffuse streaks in the net $h = 0$. (Identical in the nets $k = 0$ and $l = 0$.) (*b*) Formal representation of diffuse streaks in the net $h = 2$. (Identical in the nets $k = 2$ and $l = 2$.) (*c*) Formal representation of diffuse streaks in the net $h+l = 0$. (Identical in the nets $l+k = 0$ and $k+h = 0$.) Notice that some streaks pass right through reciprocal-lattice points of zero reflecting power. This is because the space group of the instantaneous dynamic structure is different from that of the static structure.

These figures are, of course, diagrammatic in that straight lines are shown as representing circles on the surface of the Ewald sphere.

Table 2. *Values of I from Jahn's formula*

(r constant; unit for c: 10^{11} dyne cm.$^{-2}$)

LMN →	KCl			NaCl			LiF		
lmn ↓	001	$1/\sqrt{2}\ 1/\sqrt{2}\ 0$	$1/\sqrt{3}\ 1/\sqrt{3}\ 1/\sqrt{3}$	001	$1/\sqrt{2}\ 1/\sqrt{2}\ 0$	$1/\sqrt{3}\ 1/\sqrt{3}\ 1/\sqrt{3}$	001	$1/\sqrt{2}\ 1/\sqrt{2}\ 0$	$1/\sqrt{3}\ 1/\sqrt{3}\ 1/\sqrt{3}$
100	12·7	7·7	5·1	7·9	4·9	4·1	1·56	1·2	1·3
010	12·7	7·7	5·1	7·9	4·9	4·1	1·56	1·2	1·3
001	2·7	12·7	5·1	2·0	7·9	4·1	0·83	1·56	1·3
$1/\sqrt{2}\ 1/\sqrt{2}\ 0$	12·7	3·3	5·2	7·9	2·3	3·7	1·56	0·69	0·97
$1/\sqrt{2}\ \bar{1}/\sqrt{2}\ 0$	12·7	6·9	7·2	7·9	5·4	5·6	1·56	2·6	1·7
$0\ 1/\sqrt{2}\ 1/\sqrt{2}$	5·1	10·5	5·2	3·8	5·9	3·7	1·66	1·6	0·97
$0\ 1/\sqrt{2}\ \bar{1}/\sqrt{2}$	5·1	10·5	7·2	3·8	5·9	5·6	1·66	1·6	1·7
$1/\sqrt{2}\ 0\ 1/\sqrt{2}$	5·1	10·5	5·2	3·8	5·9	3·7	1·66	1·6	0·97
$\bar{1}/\sqrt{2}\ 0\ 1/\sqrt{2}$	5·1	10·5	7·2	3·8	5·9	5·6	1·66	1·6	1·7
$1/\sqrt{3}\ 1/\sqrt{3}\ 1/\sqrt{3}$	6·6	6·2	3·5	4·8	3·6	2·4	1·65	1·15	0·43
$\bar{1}/\sqrt{3}\ 1/\sqrt{3}\ 1/\sqrt{3}$	6·6	9·9	7·6	4·8	6·0	5·6	1·65	2·14	2·05
$1/\sqrt{3}\ \bar{1}/\sqrt{3}\ 1/\sqrt{3}$	6·6	9·9	7·6	4·8	6·0	5·6	1·65	2·14	2·05
$1/\sqrt{3}\ 1/\sqrt{3}\ \bar{1}/\sqrt{3}$	6·6	6·2	7·6	4·8	3·6	5·6	1·65	1·15	2·05
	c_{11}	c_{12}	c_{44}	c_{11}	c_{12}	c_{44}	c_{11}	c_{12}	c_{44}
	3·70	0·81	0·79	4·97	1·27	1·27	12·00	4·41	6·4

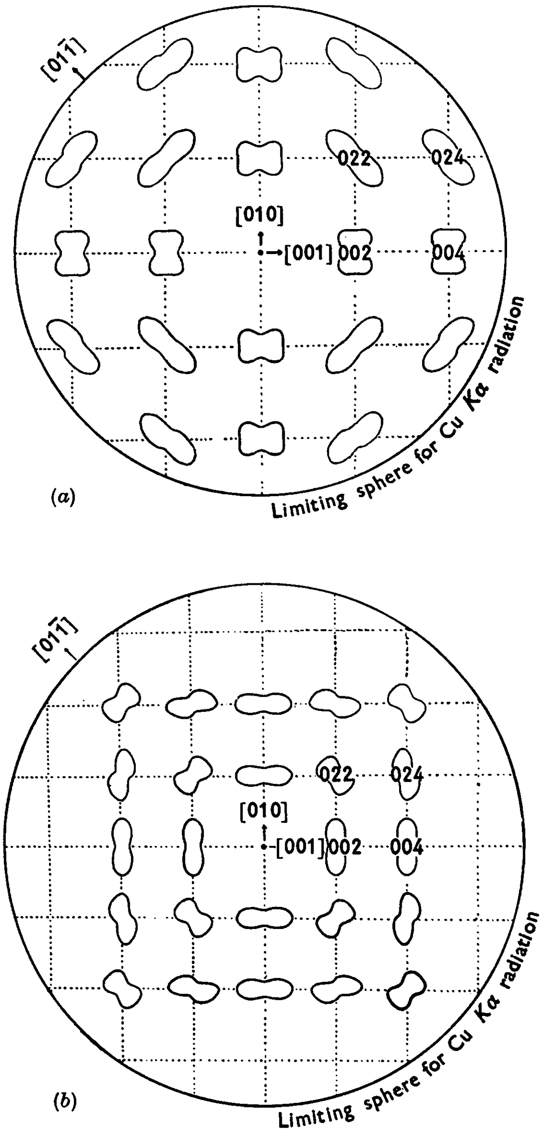

Fig. 7. (*a*) I contours in the net $h = 0$, using the elastic constants of LiF. Notice relative shapes of the contours. Compare with Fig. 2. (*b*) I contours in the net $h = 0$, using the elastic constants of NaCl. Notice relative shapes of the contours. Compare with monochromatic photograph of NaCl (Gregg & Gingrich, 1941; Guinier, 1945). Compare also with the corresponding shapes of the I contours using the elastic constants of KCl, as given by Lonsdale (1942) and those using the elastic constants of Na, as given by Jahn (1942).

monochromatizing crystal) although they could not be seen before monochromatization (Figs. 2 and 6). *These non-radial streaks were different from those found on monochromatic photographs of* KCl, since in no case did they appear along directions parallel to a cube edge in reciprocal space on the h or k or $l = 0$ nets (Fig. 6(*a*)). They corresponded to the extension of the I contours plotted using Jahn's formula, which does therefore tend to predict in which directions *strong non-radial streaks* are likely to occur for *soft crystals* having the NaCl-like structure (Fig. 7(*a*) and (*b*)).

3. X-ray diffuse scattering by a single crystal of hexamethylenetetramine

Hexamine is one of the few organic compounds crystallizing in the cubic system. It has a body-centred molecular structure. Fig. 8(*a*) shows a reciprocal-lattice representation of the X-ray diffuse scattering by a single crystal of hexamine. Agreement is observed between the equi-reflecting contours of Fig. 8(*a*) and those calculated (Fig. 8(*c*)) from the Jahn formula,

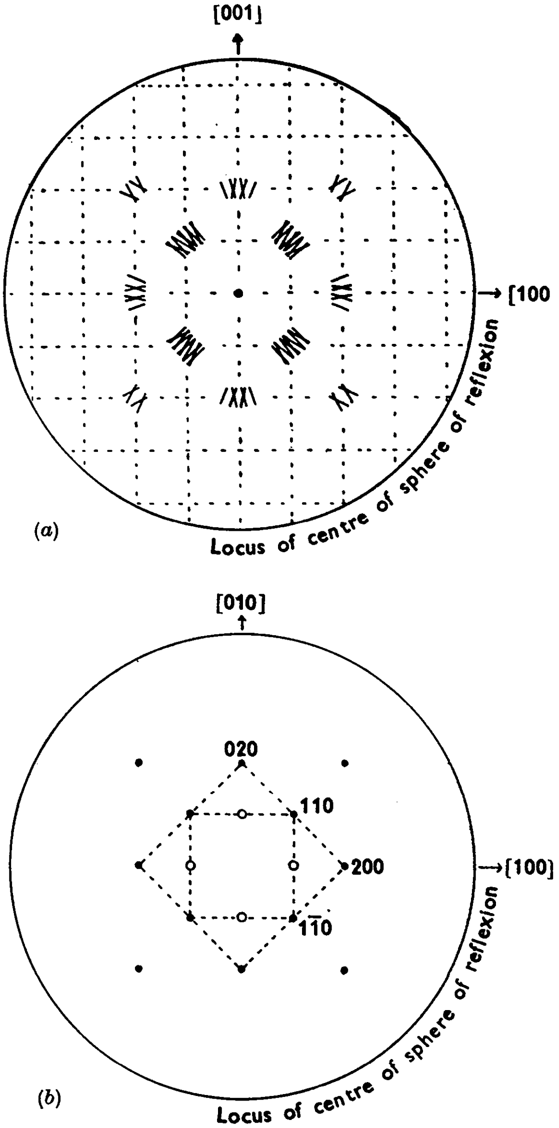

Fig. 8. (*a*) $C_6N_4H_{12}$. Cu $K\alpha$. Reciprocal net showing the positions of diffuse spots on central layer line of Laue photographs taken with the cube axis of the crystal vertical. No extension of extra reflecting power from one reciprocal-lattice point to another. (*b*) Formal representation of streaks in the net $l = 0$. (Identical in $h = 0$ and $k = 0$ nets.)

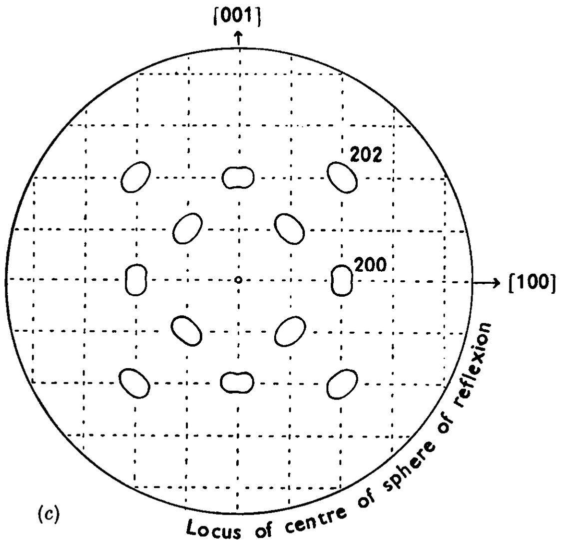

Fig. 8 (*cont.*). (*c*) Equi-reflecting contours in the net $k = 0$, using the elastic constants of hexamine. No correspondence between the Jahn contours and streak directions.

using the elastic constants of hexamine ($c_{11}=1{\cdot}5$, $c_{12}=0{\cdot}3$ and $c_{44}=0{\cdot}7\times10^{11}$ dyne cm.$^{-2}$) given by Ramachandran & Wooster (1951). But, whereas in the case of NaCl-like structures a correspondence was found between the shapes of the Jahn contours and their extension in the form of non-radial streaks, no such correspondence can be observed here (cf. Fig. 8 (*b*) and (*c*)), presumably because the streaks from a molecular crystal are mainly due to vibrations other than purely elastic ones.

4. Discussion

There is a relation between the characteristic shape of the diffuse spot and the associated non-radial streaks, which is obvious in the case of KCl and LiF, and is still valid in the case of the 'diffuse' Laue photographs for $NaClO_3$ (Fig. 3) although the symmetry of the Jahn contour is very much of an approximation in such a case. This relation between the shape of the diffuse spot and the associated non-radial streaks does not hold in the case of the molecular cubic crystal, hexamine. In such a crystal, where the closed molecule is nearly spherical, the molecule vibrates as a unit (this motion may be a rotatory or oscillatory one) and there are also vibrations of the atoms within the molecule. The latter will have frequencies much higher, in general, than those of the elastic vibrations of the lattice as a whole. The acoustical and optical frequencies may differ greatly in such a crystal, and this seems to be confirmed by the independence of diffuse-spot shapes and streak directions on monochromatic photographs of hexamine (Fig. 4).

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Photo-Elastic Properties of Crystals: Some New Results

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The non-vanishing photo-elastic constants in the C_3, S_6; C_{3h}, C_6, C_{6h}; C_4, S_4, C_{4h} crystal classes are given. Differences between them and those given earlier by Pockels for these classes are pointed out. Some interesting results, which are capable of being verified by experiment, are deduced.

1. Introduction

The author of this paper (Bhagavantam, 1942) gave a method by which group theory can be used for deriving the numbers of independent constants necessary in each of the 32 crystal classes for describing any physical property. The method, at that