



**Fig. 1** *a*, Severely degraded thin film showing 'eating traces' and growing material; *b*, less degraded, thick film with a large amount of growing material. The black dots and threads are Lithoderma; the grey areas are bryozoans. Area shown: 25 × 40 cm in both cases.

The investigation presented here stresses a problem which arises when plastics are thrown into the sea from ships. Plastics are used on ships as cargo wrappings and as ordinary plastic bags. Large sheets, thrown overboard, are not only a potential hazard to the propellers of smaller ships, but also cause trouble to fishermen who get them into their trawls. Furthermore, the films must also be considered as a source of pollution.

Our samples were provided by the crews of the LL 910 Hällö and LL 321 Sandvik, both from Smögen.

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<sup>1</sup> Holmström, A., and Sörvik, E., *J. appl. Polym. Sci.*, **18**, 761-778 (1974).

## Lattice absorption in small particles

KREIBIG and Fragstein<sup>1</sup> carried out experiments on small silver particles which showed a strong dependence of some optical properties on the particle radius. They were able to explain their results by assuming that electrons made collisions with the walls of the particle, the mean free path being equal to the particle radius.

Here I suggest that a similar effect may occur with the behaviour of phonons. With phonons in small particles of radius  $R$  we may associate an additional collision time of order, in this case,  $\tau \sim R/v$ , where  $v$  is the velocity of sound in the bulk material. If such an effect occurs an obvious means of detecting it would be in the lattice absorption of ionic solids. Ipatova, Maradudin and Wallis<sup>2</sup> have given a theoretical treatment of lattice absorption in NaCl and LiF in which they show the finite width of the absorption peak to be the result of anharmonic contributions to the potential. For NaCl they find that the damping constant  $\gamma$  and angular frequency of the peak  $\omega_0$  are related to the temperature and characteristic temperature by

$$\gamma/\omega_0 \sim 0.041/\Theta + 0.05(I/\Theta)$$

where  $\Theta \sim 370$  K,  $\omega_0 \sim 3 \times 10^{15}$  s<sup>-1</sup> for NaCl. For particles of radius  $< 10^{-6}$  cm and  $T < 10$  K, taking  $v \sim 5 \times 10^5$  cm s<sup>-1</sup>, the

effect I suggest should be easily detectable—that is, the width of the lattice absorption peak will be dominated by the collisions of phonons with the walls of the particle.

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<sup>1</sup> Kreibig, U., and Fragstein, C. V., *Z. Phys.*, **224**, 307 (1969).

<sup>2</sup> Ipatova, I. P., Maradudin, A. A., and Wallis, R. F., *Phys. Rev.*, **155**, 882 (1967)

## Lone electron pairs and stereochemistry

THE two basic assumptions of the Nyholm-Gillespie Theory<sup>1,2</sup> are, first, that valence shell electron pairs repel one another, the system adopting a minimum repulsion energy configuration (condition (i)), and second, that lone-pair-lone-pair (LL) repulsions are greater than lone-pair-bonded-pair (LB) repulsions which are, in turn, greater than bonded-pair-bonded-pair (BB) repulsions (condition (ii)). To offer a full explanation of the gross stereochemistry of all octahedral and pyramidal complexes two additional axioms are necessary: first, that lone-pair-bonded pair repulsions are less than the arithmetic mean of the lone-pair-lone-pair and the bonded-pair-bonded-pair repulsions (condition (iii)) and second, that electron pair repulsions at 120° to each other are less than half the corresponding repulsions at 90° to each other (condition (iv)). The four rules together enable a rationalisation of the stereochemistry of all known octahedral and bipyramidal complexes.

The rationale behind these assumptions can be illustrated by considering four important cases:

**The case of octahedral coordination, with two lone pairs as exemplified by XeF<sub>4</sub>, ICl<sub>4</sub><sup>-</sup>, and so on.** Experimentally, the *trans*-arrangement of lone pairs is more stable than the *cis*-arrangement (Fig. 1*a* and *b*), and the systems are square planar. In considering valence shell repulsions electron pair interactions at 180° to each other can be ignored, since they can exert no component of force perpendicular to the bond axis.

In the *trans*-arrangement (Fig. 1*a*) there are four bonded-pair-bonded-pair interactions and eight lone-pair-bonded-pair interactions, all at 90° (4BB + 8LB) whereas in the *cis*-arrangement (Fig. 1*b*) there are five bonded-pair-bonded-pair interactions, six lone-pair-bonded-pair interactions and one lone-pair-lone-pair interaction, all at 90° (5BB + 8LB + LL). In order that the *trans*-arrangement should be more stable than the *cis*-arrangement it is necessary that condition (iii) is fulfilled:

$$LB < (BB + LL)/2 \quad (1)$$

**The case of trigonal bipyramidal coordination, with one lone-pair as exemplified by SF<sub>4</sub>, SeCl<sub>4</sub>, and so on.** Two possible arrangements arise in this case, the first has C<sub>2v</sub> symmetry,

**Fig. 1** Octahedral coordination with two lone pairs, exemplified by XeF<sub>4</sub>: *a*, *trans*-arrangement; *b*, *cis*-arrangement.

