be one of the highest predicted for a photochemical reaction not involving a chain sequence.

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Habit Changes in Mixed Crystals of Phenazine and N-Oxyphenazine

WE recently measured and plotted against composition¹ the refractive indices of a complete mixed crystal series of phenazine and N-oxyphenazine, crystallized from methyl ethyl ketone. We originally thought that the crystals, which were tabular, showed the same habit, the best-developed faces being (201), but we have since found this to be a mistake. A more careful study of the morphology, using X-ray oscillation photographs, has shown that the {h0l} habit does actually change across the series (Fig. 1). Although the relative sizes of the crystal faces vary in the series, the tabular appearance is obtained at all concentrations, except in a region of poor development.

Crystals of pure phenazine (0 per cent N-oxyphenazine) nearly always have large (100) faces, though occasionally some with large (201) faces are found. Crystals containing about 28 mole per cent N-oxyphenazine are badly developed, and tend to be fibrous. X-ray photographs of two of these crystals that were sufficiently well developed showed that in one case the largest face was (201), in the other it was (001). This may indicate that there is a eutectic at or near this composition.

These results make it clear that the refractive index versus composition curve previously given for measurements made perpendicular to the *b* axis, is not a real measure of that quantity. Instead, it reflects the change in morphology as the composition varies. From the large apparent peak at about 8 mole per cent N-oxyphenazine, it is evident that only a small amount of N-oxyphenazine is sufficient to bring about a considerable change in the habit of the phenazine crystals. In this case, the crystal habit is a function of composition, as has been found with some other mixed crystal systems²⁻⁴, although in the solid-solution series of tetraphenylporphyrin and silver tetraphenylporphyrin the crystal habit was not found to be a function of composition⁵.

The measurements made parallel to the *b* axis do, however, refer to genuine refractive index changes, with

Fig. 1. {h0l} Habit changes of mixed crystals of phenazine and N-oxyphenazine. Compositions are given in terms of mole per cent N-oxyphenazine. *a*, 0 per cent; *b*, occasionally at 0 per cent; more generally up to about 28 per cent; *c*, found from about 28 to 100 per cent.

respect to the particular crystal direction [010], and show a discontinuity between about 8 and 30 mole per cent N-oxyphenazine. This lends support to the view that there is a eutectic region in this mixed crystal system.

Some crystals in this region of composition were examined microscopically at low temperature (about 80° K), but no apparent onset of inhomogeneity was observed. It would be interesting to see whether the change in morphology across the series is independent of the solvent used.

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Correlation between the Nitrogen Impurity Content and the Crystal Habit of Synthetic Diamond

THE presence of nitrogen in diamond has provided an explanation for some of the variations which are observed in the physical properties of this material¹⁻³. The nitrogen impurity can exist either as dispersed substitutional donors, in which case electron spin resonance is observed², or as non-paramagnetic aggregates of atoms³. Absorption peaks in the infrared can be obtained from nitrogen in either form⁴. Peaks at 1,129 cm⁻¹ and 1,345 cm⁻¹, coupled by a broad saddle which is peaked at 1,290 cm⁻¹, are characteristic of the paramagnetic centres. In contrast, aggregates of nitrogen give a single peak at 1,280 cm⁻¹. Dyer *et al.*⁴ have shown that the two forms of nitrogen can be distinguished even if they co-exist in a particular specimen. In most cases, however, the nitrogen exists predominantly in one form and the diamond is classified either as type Ia or as type Ib. In type Ia diamond, the aggregates of nitrogen are in a majority and in type Ib diamond the concentration of dispersed nitrogen is the larger.

In a recent survey of MBS 35/40 synthetic diamond (mean size 480μ) (manufactured by the General Electric Company) by electron spin resonance, we⁵ found that, unlike most stones which exhibited the electron resonance associated with dispersed substitutional nitrogen (type Ib), a small number of stones gave no detectable resonance. Diamonds of this type were invariably almost perfect octahedra whereas the usual habit for MBS 35/40 diamond is cubo-octahedral. The octahedra have now been examined both by electron spin resonance and by infrared spectroscopy.

Of the small number of octahedra which were available, only two were sufficiently free from inclusions to be investigated. The stones gave no observable electron resonance signal characteristic of dispersed nitrogen, while the infrared peaks associated with either the dispersed or aggregated nitrogen were scarcely detectable.

Cubo-octahedral diamonds which had previously been examined by electron spin resonance and were known to contain approximately 10¹⁷ nitrogen donors/cm³ gave infrared peaks at 1,129 cm⁻¹ and 1,345 cm⁻¹, the amplitudes of which were several times greater than the noise level.