LETTERS TO NATURE

PHYSICAL SCIENCES

Aggregation of Nitrogen in Diamond

THIS note is an attempt to make quantitative the view[1] that it is erroneous that the impurity nitrogen in diamonds is mostly located in the platelets of diamonds.

The atomic percentage (N) of nitrogen in fifteen diamonds and the absorption coefficient (μ) at 1,282 cm^{-1} have been measured[2,3] by different techniques and are

$$\mu_{1,282} = (300 \pm 20)N \text{ cm}^{-1} \quad (1)$$

for

$$4 \times 10^{-3} < N < 2{\cdot}5 \times 10^{-1} \quad (2)$$

The only exception among the fifteen crystals was slightly inhomogeneous and had a small N. Sobolev *et al.*[1] found that the absorption coefficient at 1,368 cm^{-1} is proportional to the intensity of the X-ray diffraction spike that is caused by condensations, or platelets, in the cube planes[4]. The proportionality constant was not determined. Both these correlations hold over at least the ranges

$$1{\cdot}3 < \mu_{1,282}/\mu_{1,368} < 30 \ \ (2, 3) \quad (3a)$$

$$0{\cdot}2 < \mu_{1,282}/\mu_{1,368} < 12 \ \ (1) \quad (3b)$$

These data were taken on natural transparent diamonds apparently of types I*a* and II*a*. The rare type I*b* diamond (about 0·1 per cent of clear diamonds[5]) is assumed not to complicate the data.

It is known that there is a negligible concentration of paramagnetic isolated or almost isolated nitrogen in these types[6-8]. The bulk of the nitrogen must therefore exist in other forms such as in the platelets, in smaller aggregates, or in an isolated non paramagnetic form. We assume that the platelets contain nitrogen and, initially, that the nitrogen may exist in only one non platelet form. The correlations above may then be fulfilled subject to one of two conditions: either both the platelet and non platelet forms give absorption at 1,282 cm^{-1} in proportion to the number of atoms in those forms, or, if this is not so, one form of the nitrogen must account for the bulk of the nitrogen.

We consider first the former possibility. The strongest 1,368 cm^{-1} absorption on record[1] is about 25 cm^{-1} in a diamond with $\mu_{1,282} = 5$ cm^{-1}, implying, from (1), a total nitrogen content of 0·06 per cent. Hence the concentration of nitrogen in platelet form is, at most, $N_p = \mu_{1,368}/1,500$ per cent, where $\mu_{1,368}$ is measured in cm^{-1}. Then, for diamonds in which $\mu_{1,368} \sim 0{\cdot}5\ \mu_{1,282}$, as is often the case (see Fig. 2 of ref. 3), at most 10 per cent of the nitrogen is in platelet form.

The latter possibility can only satisfy (1) and (3) if the dominant form of the nitrogen is that giving the 1,282 cm^{-1} band. A figure may be put on the degree of domination required by noting that if a specimen has a 1,282 cm^{-1} absorption lower than that predicted by (1) we would ascribe the difference to the presence of nitrogen in platelet form. If the 1,282 cm^{-1} absorption measured is higher than (1), the difference must be due to experimental error. In no specimen has the 1,282 cm^{-1} absorption been measured significantly low (Fig. 4 of refs. 2 and 3) so that at the most the nitrogen in platelet form is 5 to 10 per cent of the total present, for the specimens within the limits of (3*a*) at least.

To distinguish between the two conditions it is necessary to know the absorption at 1,282 cm^{-1} per nitrogen atom for the two forms of nitrogen. Calculations are unreliable because no detailed models for the centres have been confirmed. The temperature independence of most of the impurity induced infrared bands[9] implies a lack of anharmonicity in the vibrational potential and hence uniaxial stress measurements are unlikely to determine the symmetry of the nitrogen forms. As observed in Si[10-13], different defects in diamond may stimulate the same perfect lattice modes. Thus all the neutron induced one photon bands[14] have the same shape and energy (although different relative intensities) as impurity bands in type I*a* diamond, many of which, in turn, may be associated with peaks in the perfect lattice density of phonon states[15]. Some bands in Si[10-13], however, are characteristic resonances of a defect. This characterization is shown in diamond by the failure of irradiation damage to create either the 1,282 cm^{-1} or the localized 1,368 cm^{-1} band[14]. So, although in principle the platelets could vibrate at 1,282 cm^{-1} with an absorption satisfying equation (1), it is unlikely.

We have demonstrated that existing data show that at least 90 to 95 per cent of the nitrogen in diamonds satisfying equation (3*a*) is in an unknown non platelet form if, as seems likely, the platelets cannot give absorption at 1,282 cm^{-1}. If the platelets do absorb at 1,282 cm^{-1} then the fraction of nitrogen in platelet form is at most $0{\cdot}2\ \mu_{1,368}/\mu_{1,282}$ and the non platelet form is again usually dominant. This still leaves sufficient nitrogen to be present in many other forms, including platelets at their known concentration[16]. The arguments given may be readily generalized to allow for several aggregated forms, but the conclusions are unaltered.

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Correlations between Earth's Gravitational and Magnetic Field

IN a recent communication Hide and Malin[1] studied the similarities in the variations of Earth's gravitational and magnetic fields in an effort to determine the undulations on the core-mantle interface. These undulations, if present, can produce significant distortions in the geomagnetic field as it is observed on the Earth's surface[2,3]. These bumps will also distort the gravitational field.