REORIENTATIONS OF NITROGEN IN DIAMOND

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Abstract: Stress-induced ordering of substitutional nitrogen in Type Ib natural diamond was observed in electron paramagnetic resonance. The degree of alignment was measured as a function of the applied stress. The relaxation times for ordering were determined from annealing experiments.

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BY applying uniaxial stress to a Type Ib natural diamond, the substitutional nitrogen centres in the crystal are aligned. This stress-induced ordering is directly observable in the electron paramagnetic resonance spectrum associated with these centres. In the work reported below, the degree of ordering was measured as a function of the applied stress. From the results it is concluded that the Jahn-Teller stabilisation energy of the nitrogen centres is large. Using an isothermal procedure the stress-induced ordering was annealed. The lower activation energy, found for the relaxation times, indicates that the mechanism for reorientation of centres differs from that previously reported for higher temperatures.

1. Electronic structure

Substitutional nitrogen distributed as isolated centres through diamond is the predominant chemical impurity present in Type Ib crystals. Associated with the centre is a donor level in the diamond band gap at a position about 2 eV below the conduction band edge⁽¹⁾. In the neutral charge state the donor electron is bound to the nitrogen atom in an anti-bonding orbital. This orbital extends primarily between the nitrogen atom and one of its four nearest-neighbour carbon atoms. In order to accommodate the extra electron with minimum energy, the length of the bond increases. This implies a distortion of the centre, as illustrated in Fig 1. The distortion is a manifestation of the Jahn-Teller instability⁽²⁾. The symmetry of the centre is reduced from cubic (point group $\bar{4}3m$) to trigonal (point group 3m). The 3-fold symmetry axis is along a <111> crystallographic direction. Consequently, for a given lattice site of the nitrogen atom, four different orientations of the centre are possible. If no strains and impurity interactions are present, these are equivalent in energy. They therefore occur with equal probability. For reference purposes the four nearest-neighbour carbon positions of the nitrogen atom are labelled a, b, c, and d, as shown in Fig 1.

2. Electron paramagnetic resonance

The neutral centre possesses an odd number of electrons. Because of the one unpaired spin, residing primarily in the anti-bonding orbital, the defect is paramagnetic with $S = \frac{1}{2}$. The hyperfine interaction with ^{14}N, which has nuclear spin $I = 1$ and a natural abundance of 99·63%, is well resolved in electron paramagnetic resonance (EPR). The spectrum, known as the Pl-spectrum, was first reported by Smith and co-workers⁽³⁾ and later studied in more detail by Loubser and du Preez⁽⁴⁾.

The spin-Hamiltonian describing the main features of the spectrum is:

$$H = \mu_B \vec{S}\cdot\overleftrightarrow{g}\cdot\vec{B} + \vec{S}\cdot\overleftrightarrow{A}\cdot\vec{I}. \qquad (1)$$

The coupling tensors, Zeeman splitting tensor $\overleftrightarrow{g}$ and hyperfine interaction tensor $\overleftrightarrow{A}$, must reflect the <111>-axial symmetry of the centre. However, because of the small value of the spin-orbit interaction in carbon and nitrogen, the $\overleftrightarrow{g}$-tensor is found to be isotropic within experimental accuracy: its principal values are $g_{//} = g_{\perp} = 2{\cdot}0024 \pm 0{\cdot}0002$⁽⁵⁾. Using electron-nuclear double resonance, Cook and Whiffen⁽⁶⁾ were able to determine the components of the hyperfine interaction tensor with great accuracy. They found $A_{//} = 114{\cdot}034$ MHz and $A_{\perp} = 81{\cdot}325$ MHz, corresponding to splittings of 4·067 mT and 2·902 mT, respectively, in the EPR experiment. The energy levels E are given by

$$E(m_S, m_I) = g\mu_B B m_S + A(\theta,\varphi) m_S m_I, \qquad (2)$$

with $m_S = \pm\frac{1}{2}$, $m_I = -1, 0, +1$; and (θ,φ) specifying the direction of the magnetic field B. The resonance condition following from the selection rules $\Delta m_S = \pm 1$, $\Delta m_I = 0$, is

$$h\nu = \Delta E = g\mu_B B + A(\theta,\varphi) m_I. \qquad (3)$$

The expression shows that angular dependence, arising from the anisotropy in the hyperfine interaction, will not be present in the central line for which $m_I = 0$. It will, however, be present for the transitions with $m_I = \pm 1$. Fig 2 shows the angular dependence observed when the magnetic field $\vec{B}$ is rotated in the $(0\bar{1}1)$-plane of the crystal. The effective value $A(\theta,\varphi)$ of the hyperfine interaction depends on the angle between the magnetic field $\vec{B}$ and the principal axes of the $\overleftrightarrow{A}$-tensor, which are fixed with

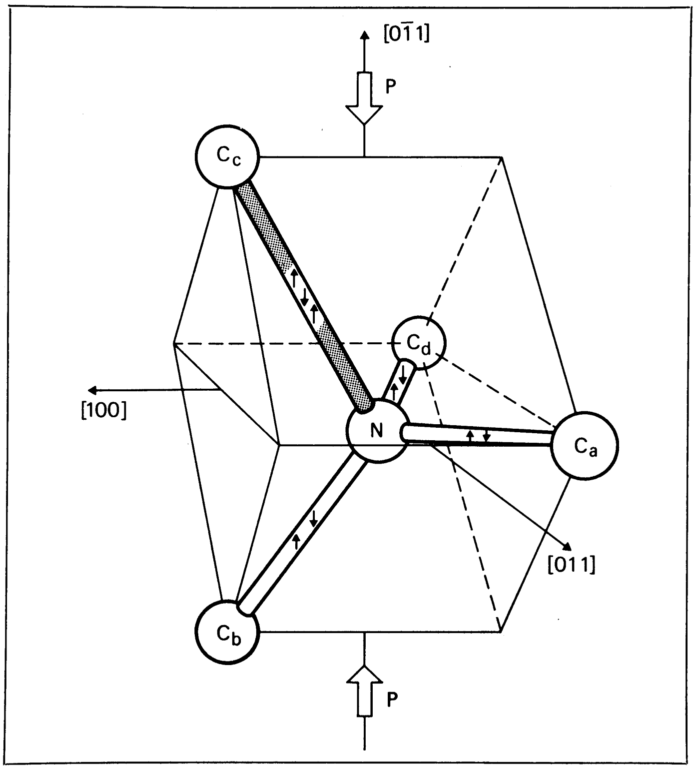


Fig 1 *Model of substitutional nitrogen in diamond in the orientation labelled c. Also shown are axes defining the coordinate system and compressive stress* $\vec{P}$ *along* $[0\bar{1}1]$

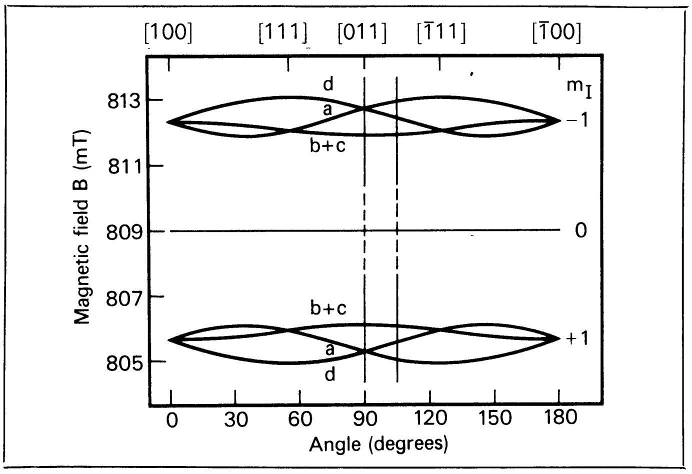


Fig 2 *Resonance fields for the P1 EPR spectrum of neutral substitutional nitrogen in diamond. Angular dependence for rotation of the magnetic field in the* $(0\bar{1}1)$ *plane of the crystal. Curves are labelled with the corresponding defect orientations. The vertical lines at 90° and 105° indicate the scans of the magnetic field for the spectra shown in Fig 3 and 4*

respect to the defect. The splitting will therefore be different for the defect orientations a, b, c, and d. For the specific choice of the magnetic field in the $(0\bar{1}1)$-plane, the angles between $\vec{B}$ and the defect axes of the orientations b and c are always equal. As a consequence the resonances from these two orientations will coincide at all angles. (It may be mentioned that if the nitrogen atom is situated on the other fcc sub-lattice of the diamond structure, the four possible orientations of the centre are oppositely directed compared to a, b, c, and d, and may be labelled $\bar{a}$, $\bar{b}$, $\bar{c}$, and $\bar{d}$. Since the inversion and the translation operations are not detectable in EPR, the resonances from centres in orientations a and $\bar{a}$, b and $\bar{b}$, etc., always coincide pairwise. For ease of discussion the centres in the orientations $\bar{a}$, $\bar{b}$, $\bar{c}$, and $\bar{d}$ are therefore omitted in this text).

Actual EPR measurements were performed in a superheterodyne K-band spectrometer, microwave frequency $\nu \simeq 23$ GHz, tuned to observe the dispersive part χ' of the magnetic susceptibility. Details of the equipment are given by Sieverts(7). In the present experiments the EPR spectra were recorded with the sample at the temperature $T = 142$ K.

An EPR spectrum for $\vec{B}//[011]$ is shown in the upper part of Fig 3. The central part of the spectrum, only one isotropic line, is left out as it is of no interest in the following discussion. Two resonances are observed, both for $m_I = +1$ and $m_I = -1$, corresponding to centres in orientations a+d and b+c. For a magnetic field rotated 15° away from [011] in the $(0\bar{1}1)$-plane three resonances are observed, as shown in Fig 4 (upper part). In agreement with Fig 2 these are labelled with the defect orientations a, d, and b+c. These examples show that resonances arising from the different defect orientations are well resolved. The orientations can therefore be monitored individually in EPR. The amplitudes of the resonance lines are assumed

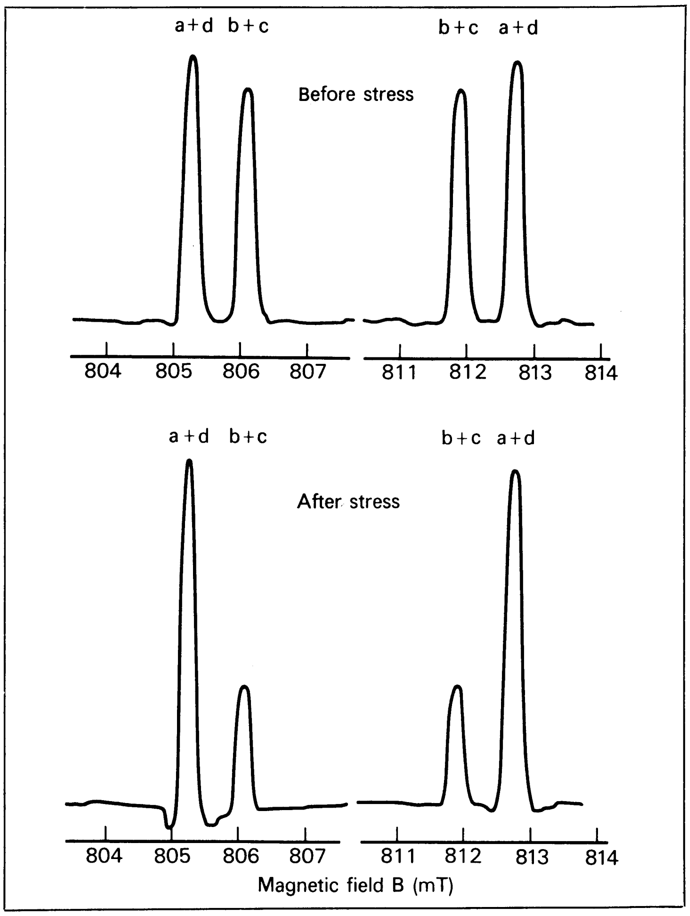


Fig 3 *EPR spectrum of neutral substitutional nitrogen in diamond for* $\vec{B}//[011]$ *at* $T = 142$ *K, the spectrum before, and the spectrum after inducing alignment by a uniaxial stress* $|\vec{P}| = 1{\cdot}65$ *GPa along the* $[0\bar{1}1]$ *direction. The central part of the spectrum* $(m_I = 0)$ *is omitted*

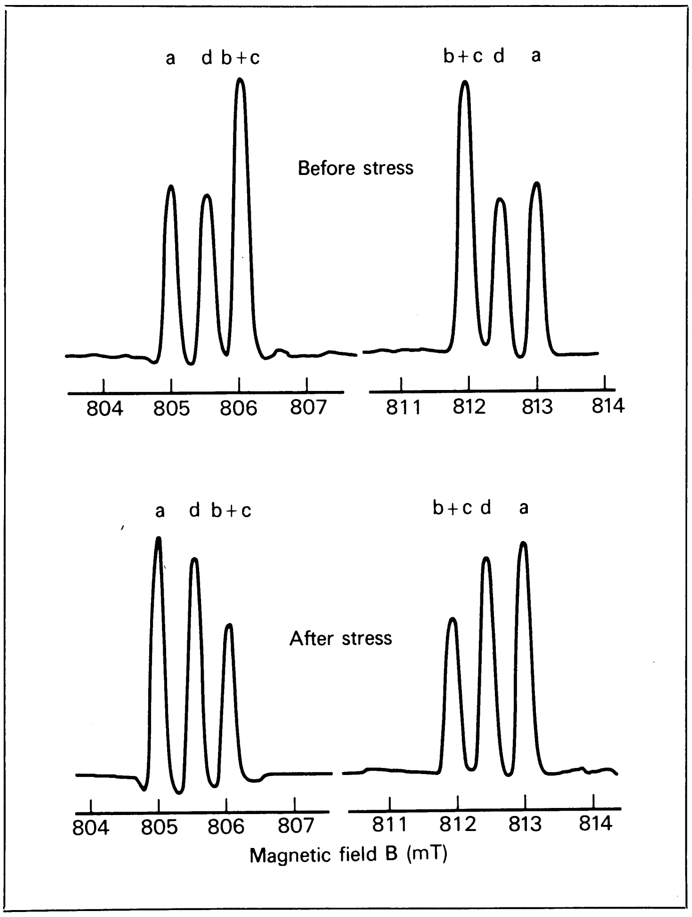


Fig 4 *EPR spectrum of neutral substitutional nitrogen in diamond for* $\vec{B}//[011] + 15°$ *in the* $(0\bar{1}1)$ *plane at* $T = 142$ *K, the spectrum before, and the spectrum after inducing alignment by a uniaxial stress* $|\vec{P}| = 1{\cdot}65$ *GPa along the* $[0\bar{1}1]$ *direction. The central part of the spectrum* $(m_I = 0)$ *is omitted*

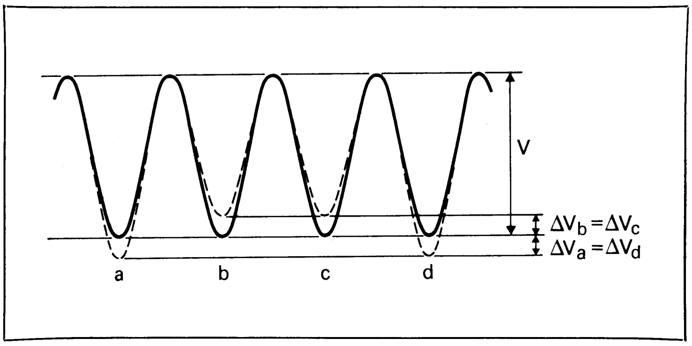
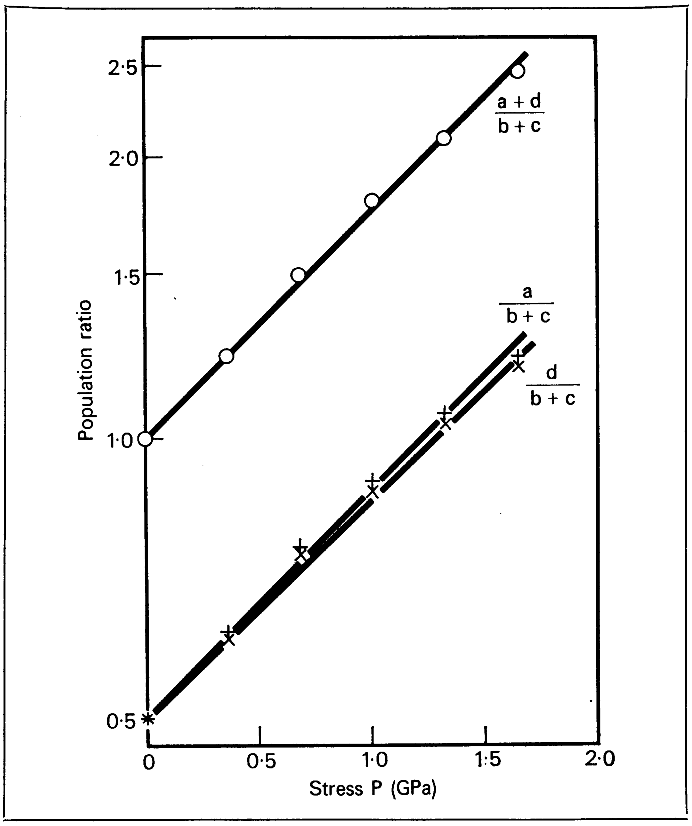


Fig 5 Left *Schematic representation of the potential barriers separating the nitrogen centre in the orientations a, b, c, and d without stress (full curve) and with stress* $\vec{P}//[0\bar{1}1]$ *(dashed curve)*

Fig 6 Below *Ratio of the populations of the nitrogen orientations after alignment as a function of uniaxial stress* $\vec{P}$ *along* $[0\bar{1}1]$



to be proportional to the concentrations of the centres in the corresponding orientations. For a random distribution the intensities of the lines should be equal or should differ by a factor of 2. The small deviations from these simple ratios, apparent in the upper parts of Fig 3 and 4, do not reflect real population differences. At higher temperatures, where spin relaxation times are shorter and saturation effects are less, similar deviations in the resonance amplitudes are absent.

3. Stress-induced reorientations

The energy equivalence of the various orientations is destroyed when uniaxial stress is applied to the crystal. This is illustrated schematically in Fig 5 for compressive stress in the $[0\bar{1}1]$ direction. Stress in this direction causes compression of the bond lengths in the b- and c-directions, while the a- and d-bonds are elongated. Consequently the energy of centres in the orientations b and c is raised relative to the energy of the a- and d-orientations. Any uniform shift of the energies arising from the hydrostatic component in the strain is omitted from Fig 5 as it is of no interest for reorientation processes. At sufficiently high temperatures, reorientations of the centres will occur by thermally activated jumps across the potential barriers separating the orientations. The reorientations will take place at a rate determined by the thermal energy kT and the barrier height V. With stress present, the centres will redistribute over the four orientations. When equilibrium is established there will be a Boltzmann distribution. For the case considered, the concentrations n_i (i = a,b,c,d) of the four orientations will satisfy $n_a = n_d > n_b = n_c$. The effect is called stress-induced ordering or alignment.

In the actual experiment, alignment was studied in a Type Ib natural diamond crystal (sample 99 of ref.8) with an isolated substitutional nitrogen concentration of $\Sigma n_i \simeq 7 \times 10^{18}$ cm^{-3} as inferred from infrared absorption. Uniaxial stress was applied parallel to $[0\bar{1}1]$ at a sample temperature T = 213 K. After a time of 10 minutes an equilibrium distribution of defects was reached. With the stress still applied the sample was quickly cooled to T = 142 K. The stress was then removed and the EPR spectra measured at the latter temperature. At this low temperature the alignment is essentially frozen in. EPR spectra of the diamond with the nitrogen centres aligned by stress are shown in the lower parts of Fig 3 and 4. On comparing them with the upper parts of these figures the enhancement of the signals from orientations a and d, with the simultaneous reduction of the (b+c) resonance, is evident. As the intensities of the resonances are assumed to be proportional to the concentrations of centres causing them, the EPR results allow for a quantitative study of the reorientation phenomena.

In order to analyse the reorientation effect, the quantity Ξ is introduced by the relation $\Xi = \Delta V_i/\varepsilon_i$. For small stresses the energy shifts ΔV_i will be linear to the strains ε_i. The constant Ξ is the energy shift of a defect per unit strain. The strains ε_i are those along the defect axes. These strains are thought to be most relevant as the bond in this direction accommodates the donor electron. For easier visualisation of the results, this more physical treatment is preferred to a more mathematical one using the elastic dipole tensor(9). For stress $\vec{P}$ along $[0\bar{1}1]$ one may derive $\Delta V_a = -\Delta V_b = -\Delta V_c = \Delta V_d = -\Xi S_{44}P/6$, where S_{44} is an elastic compliance constant of diamond. In equilibrium, when a Boltzmann distribution is established, the populations are given by $n_a = n_d$, $n_b = n_c$, and $\ln(n_a/n_b) = \Xi S_{44}P/3kT$. The temperature at which the alignment is frozen in determines T. With the quick cooling as mentioned, T will be 213 K. For compressive stresses, as applied in the present experiment, the stress P has negative value.

The alignment was experimentally studied as a function of stress for values $|\vec{P}|$ up to 1·65 GPa. Results are presented in Fig 6. The upper curve is derived from the measurements with $\vec{B}//[011]$, the lower ones are from the measurements with $\vec{B}$ rotated 15° away from $[011]$. To eliminate drifts in the spectrometer sensitivity, only intensity ratios within the EPR spectra were considered in the analyses. The equilibrium concentrations for zero stress were normalised in order to eliminate the small deviations in amplitudes mentioned at the end of section 2. The same normalisation factors were used in the analyses of measurements with alignment present. The straight lines in Fig 6, obeying the relationship derived above, were obtained

Fig 9 Right *EPR spectra of neutral substitutional nitrogen in natural diamond for* $\vec{B}//[011]$. *The central line* ($m_I = 0$) *and the hyperfine component corresponding to smaller magnetic fields* ($m_I = +1$) *are shown for temperatures in the range* $452\ K \leqq T \leqq 870\ K$ (*After Shul'man* et al(12))

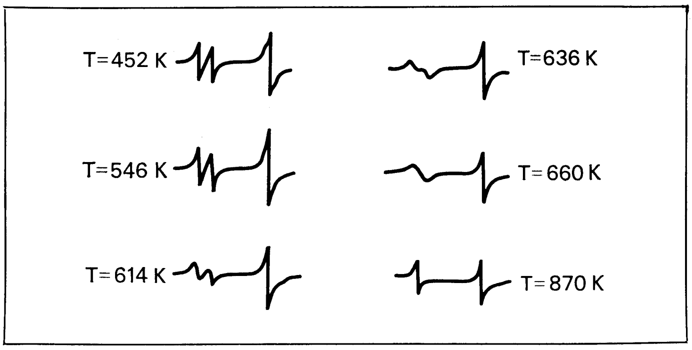
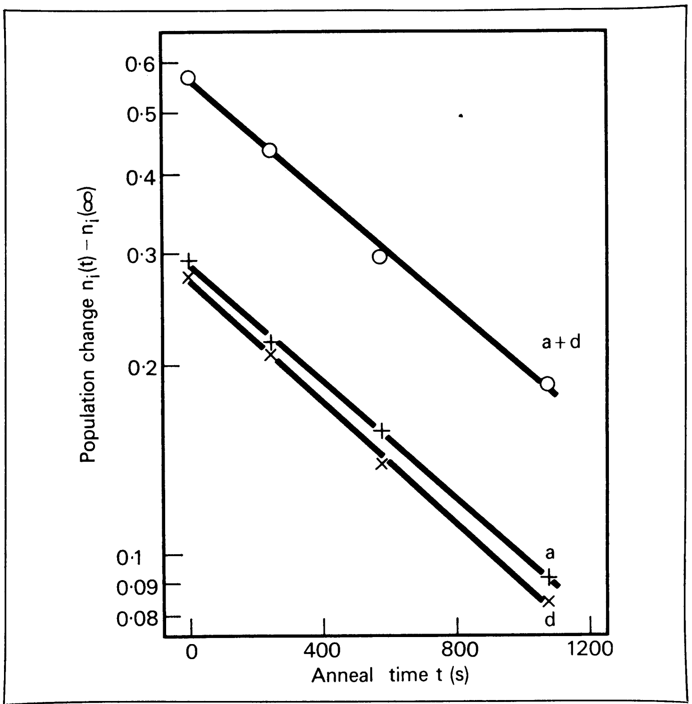


Fig 7 Below *The anneal of stress-induced ordering (at 1·00 GPa) as a function of time in the isothermal anneal treatment at* $T = 189\ K$



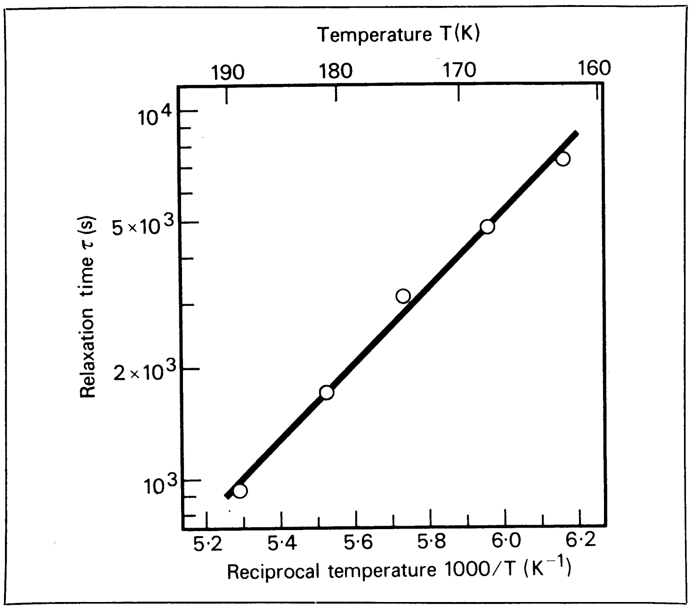


Fig 8 *The relaxation time for anneal of stress-induced ordering as a function of anneal temperature as obtained from the static experiments at low temperatures*

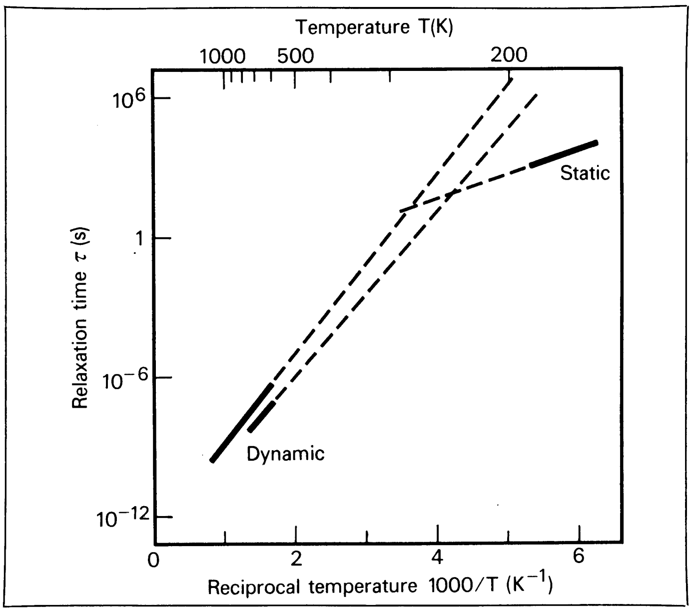


Fig 10 *The relaxation time for anneal of stress-induced ordering as a function of anneal temperature. The results from static experiments at low temperatures and those of dynamic experiments at high temperatures*(12,13) *are represented*

by least squares fitting to the experimental data. From their slopes, and using $S_{44} = 1{\cdot}74 \times 10^{-12}\ Pa^{-1}$(10), the value $\Xi = -18$ eV is calculated.

The minus sign in the value of Ξ is consistent with the model where the defect energy decreases when the bond length increases. Previously, estimates of the amount of distortion of the nitrogen centre have been given. By considering overlap between orbitals and bond angles, Smith *et al*(3) arrive at an increase in the bond length by about 10%. In a theoretical treatment, using the extended Hückel theory, Messmer and Watkins(11) found minimum energy of the nitrogen centre for a distortion of +25%. Distortions are thus expected to be substantial. In combination with the value of Ξ they lead to appreciable lowering of the energy. The Jahn-Teller stabilisation energy is large. This also explains the deep level nature of the nitrogen donor in diamond. Calculations on the defect must take the relaxation into account. They are otherwise of limited practical value.

4. Thermally-induced reorientations

4.1. Static effects at low temperatures

At elevated temperatures, without stress applied, the stress-induced ordering will anneal. Thermally activated reorientations will restore the random distribution of centres over the four possible orientations. This randomisation was studied as a function of anneal time using an isothermal annealing procedure. Because of the low concentration of nitrogen impurities, they behave as isolated centres. One therefore expects first order kinetics, with the change of populations n_i as a function of time t being governed by

$$dn_i/dt = -\{n_i(t) - n_i(\infty)\}/\tau. \tag{4}$$

The solution reads:

$$\{n_i(t) - n_i(\infty)\} = \{n_i(0) - n_i(\infty)\} \exp(-t/\tau). \tag{5}$$

A typical result, obtained for the anneal temperature T = 189 K, is shown in Fig 7. The relaxation times τ were determined from the slopes of the least-squares-adjusted straight lines. The isothermal anneal studies were performed at five temperatures in the interval $162\ \mathrm{K} \leqq T \leqq 189\ \mathrm{K}$. In Fig 8 the relaxation times are represented as a function of the reciprocal of the temperature. The results may be fitted by an Arrhenius-type expression

$$\tau = \tau_0 \exp(E/kT).$$

The straight line in Fig 8 represents such a fit, with $\tau_0 = 3 \times 10^{-3}$ s and $E = 0{\cdot}20$ eV. Because of the rather narrow temperature range in which measurements were carried out, the fit is quite satisfactory, although the experimental points indicate some curvature.

4.2. Dynamic effects at high temperatures

On increasing the temperature the reorientation rate will increase monotonously. When the reorientation frequencies become comparable to differences in the hyperfine splittings, the shape of the resonance lines will be affected. Line broadening occurs for frequencies around 10 MHz. At still higher temperatures, when reorientation frequencies of ≃ 1 GHz are much larger than those corresponding to differences in the hyperfine splitting, one resonance is observed at the average position of the previously separated components. Such studies of motional effects were carried out by Shul'man and co-workers(12) and also by Loubser and van Ryneveld(13). Fig 9, which is taken from the work of Shul'man *et al*, shows the effect of rapid reorientations on the EPR spectrum. These effects can be described in a way analogous to the hindered rotation of molecular complexes. Using the theory developed for these processes(14) the reorientation rate can be obtained from an analysis of the observed line shapes and positions. On fitting the results to an Arrhenius expression, the parameters found were as given in Table 1. A graphical representation of the high and low temperature results is given in Fig 10. The comparison of results for both temperature ranges reveals that the mechanism underlying reorientation is different. This is a subject of further study◊

TABLE 1
Relaxation time parameters of substitutional nitrogen in diamond

τ_0 (s)	E (eV)	*Temperature range* (K)	*Reference*
10^{-13}	0·7	600 – 750	(12)
$2{\cdot}5 \times 10^{-13}$	0·76	600 – 1230	(13)
3×10^{-3}	0·20	162 – 189	this work

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