

12. STRESS-INDUCED REORIENTATIONS OF NITROGEN IN DIAMOND

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Introduction. Isolated substitutional nitrogen, as occurring in type Ib diamonds, is normally a neutral impurity. The donor electron occupies an antibonding orbital between the nitrogen atom and one of the nearest-neighbour carbon atoms. As there are four nearest neighbours to the nitrogen atom, a fourfold orbital degeneracy would exist. A lowering of the energy arises from a spontaneous distortion of the center from T_d to C_{3v} symmetry, with the 3-fold axis parallel to $\langle 111 \rangle$. A distorted nitrogen center can be accommodated in the host lattice in four different orientations, which are energetically equivalent.

This orientational degeneracy is lifted by applying uniaxial stress. The energy of a center is raised if a compressive stress is (mainly) parallel to the bond with the donor electron. Likewise, the energy is lowered for compression perpendicular to that bond. Reorientations of the nitrogen centers are possible if the temperature is sufficiently high that the potential barriers between the defect orientations can be surmounted. Under a uniaxial stress a Boltzmann distribution will be established with an increased occupation of energetically favourable orientations, and with less centers in the orientations with high energy.

Unionized nitrogen in diamond is a paramagnetic center because of the unpaired spin in the antibonding orbital. The spin-Hamiltonian parameters describing the associated electron paramagnetic resonance (EPR) are $g=2.0024$, $A_{\parallel}=4.067\text{mT}$, and $A_{\perp}=2.902\text{mT}$ ^(1,2). Because of the anisotropy in the hyperfine interaction with the nitrogen nucleus ($^{14}\text{N}:I=1$) separate resonances are observed for each of the four orientations of the center. These can be well resolved for $m_I=\pm 1$ but for the central line, $m_I=0$, they all coincide. The amplitudes of the resonances are proportional to the number of centers from which they originate. Alignment, i.e. preferential occupation of some orientations, can be monitored in EPR.

Stress-induced alignment. Reorientation experiments on the nitrogen center were performed using one natural type Ib diamond and uniaxial compressive stress with values up to 1.65 GPa. The stress was applied parallel to the $[0\bar{1}1]$ -direction, for a sufficient time to reach saturation of alignment at the sample temperature of 213K. With the stress removed after cooling the diamond to 142K, EPR spectra were measured for $\vec{B}//[011]$ and $\vec{B}//[011] + 15^\circ$ in the $(0\bar{1}1)$ -plane. It was found that the population of the orientations $a=[111]$ and $d=[\bar{1}\bar{1}\bar{1}]$ increases with the stress by depopulation of the orientations $b=[\bar{1}\bar{1}1]$ and $c=[1\bar{1}\bar{1}]$. To analyze the results it is assumed that the energy change of a center is proportional to the fractional change in length of the bond which accommodates the donor electron. Defining the proportionality constant as E , the relation $\ln\{(n_a+n_d)/(n_b+n_c)\} = Es_{44}P/3kT$ can be derived (n_a =number of centers in orientation a, etc., s_{44} = elastic compliance constant, P =stress, k =Boltzmann constant, T =temperature at which alignment is frozen in). This dependence of the population ratio on stress is observed experimentally, as shown in figure 1. The regression lines through the experimental points correspond to $E=-17\text{eV}$. The minus sign is consistent with the defect model that the length of the bond accommodating the extra electron is increased.

Anneal of alignment. At elevated temperatures, without stress applied, the stress-induced alignment will disappear. This randomization of the distribution of centers among the four possible orientations was studied by an isothermal annealing procedure. The anneal follows first order kinetics: the dependence on time t is given by $\{n(t)-n(\infty)\} = \{n(0)-n(\infty)\}\exp(-t/\tau)$. The relaxation time constants τ were determined for temperatures in the range 162-189K. The constants τ_0 and E in the Arrhenius expression $\tau=\tau_0\exp(E/kT)$ were adjusted to the experimental data by least squares fitting. The present results, for one diamond only, are substantially different from data published by Loubser, et al ⁽³⁾ and Shul'man, et al ⁽⁴⁾, as shown in Table I. The latter data were obtained by observing motional effects on the EPR spectrum of the nitrogen center at high temperatures.

References

1. W.V. Smith et al. Phys. Rev. 115, 1546 (1959).
2. R.J. Cook & D.H. Whiffen, Proc. Roy. Soc. A295, 99 (1966).
3. J.H.N. Loubser & W.P. van Ryneveld, Br. J. Appl. Phys. 18, 1029 (1967).
4. L.A. Shul'man et al. Soviet Physics-Solid State 8, 1842 (1967).

Table I. Comparison of results for reorientation
of the nitrogen center

τ_0 (s)	E (eV)	Temperatures (K)	Reference
2.5×10^{-13}	0.76	600-1230	3
10^{-13}	0.7	600- 750	4
3×10^{-3}	0.20	162- 189	this work

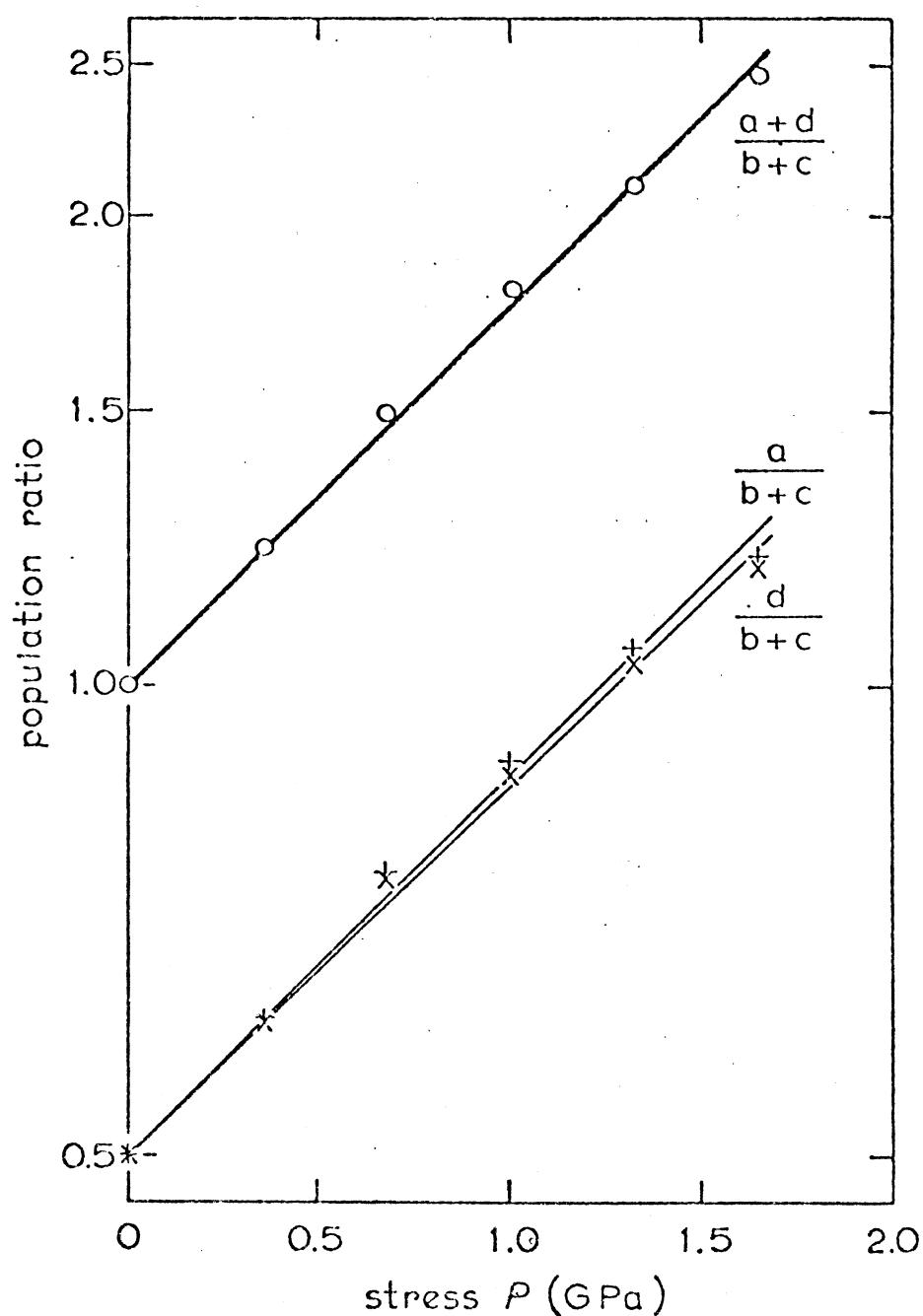


Fig. 1. Ratio of the
populations of the
nitrogen orientations
a, b, c, and d after
alignment by uniaxial
stress P along $[0\bar{1}1]$.