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Reorientation of Nitrogen in Type-Ib Diamond by Thermal Excitation and Tunneling

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The rate of anneal of stress-induced ordering of isolated substitutional nitrogen impurities in diamond, measured in the temperature range $78\text{ K} < T < 200\text{ K}$, shows large deviations from Arrhenius-type behavior. It is concluded that in the temperature range considered, reorientation of the centers occurs by tunneling between thermally populated excited vibrational states. Two parameters serve to describe reorientations by thermal activation, by tunneling, and by the combined process.

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In type-Ib diamond the dominant impurity nitrogen is present as singly isolated atoms occupying substitutional lattice sites. The nitrogen atoms do not occupy the regular sites in the lattice, but are displaced along a $\langle 111 \rangle$ direction away from one of their four nearest-neighbor carbon atoms. For a given site of the nitrogen atom four different directions of relaxation are available. The distortion of the center from cubic to trigonal symmetry has been considered over many years to be a consequence of the Jahn-Teller instability^{1,2} associated with a triply degenerate band-gap level. More recently it was pointed out that the unpaired electron occupies an A_1 singlet band-gap level. The observed distortion cannot be described by a simple Jahn-Teller effect, but is the result of strong chemical rebonding.³ However, these different interpretations do not influence our analysis. Because of the distortion the nitrogen has a deep donor level, at about 2.2 eV below the conduction band,⁴ and is not thermally ionized. In the neutral charge state the center is paramagnetic and has been observed in EPR⁵⁻⁷ and electron-nuclear double resonance (ENDOR).⁸ By these measurements the atomic constitution and symmetry of the center was unambiguously determined. In the EPR spectra the four orientations of the center in the host crystal are individually observable as they have different hyperfine interactions with the central nitrogen nucleus (¹⁴N: nuclear spin $I=1$, natural abundance 99.63%). If no strains or impurity interactions along preferred directions are present the four defect orientations are equivalent in energy. In equilibrium they will therefore occur with equal probability. The energetic equivalence of the defect orientations can be lifted by applying external

uniaxial stress to the diamond crystal. A stress-induced ordering of the impurities, or alignment, will be established. This phenomenon can be quantitatively monitored with use of EPR.⁹

In the experiment reported in this paper, alignment of nitrogen centers in diamond was induced by applying uniaxial compressive stress with values up to 2 GPa. This results in an increase up to 50% of the concentrations of energetically favorable orientations with a related shortfall of the higher-energy orientations. On removing the stress the isothermal anneal of nonequilibrium population was measured. In nearly all cases a simple exponential decay, corresponding to first-order kinetics, was observed. The time constants governing the rate of anneal were determined at various temperatures T in the range $78 < T < 200\text{ K}$. In the experiments four type-Ib samples were used. Three of these, N1 to N3, were natural diamonds, whereas sample S1 was a synthetic diamond. The nitrogen concentrations in the sample were determined by the absorption at $8.85\ \mu\text{m}$,¹⁰ and found to be about $6 \times 10^{24}\ \text{m}^{-3}$ for the natural diamonds and $4 \times 10^{25}\ \text{m}^{-3}$ for sample S1. In the samples N1, N2, and S1 the impurity alignment was induced by a stress $\vec{P} \parallel \langle 011 \rangle$; in the experiments with sample N3 the stress was applied parallel to $\langle 111 \rangle$. As expected, a stress $\vec{P} \parallel \langle 100 \rangle$, applied to sample S1 in an additional experiment, did not produce any measurable alignment. Results for the reorientation relaxation time constant τ as a function of temperature are given in Fig. 1. The curvature in the plot demonstrates that an Arrhenius law is not obeyed. The deviation from thermally activated behavior becomes even more apparent when the present results are combined with those of pre-

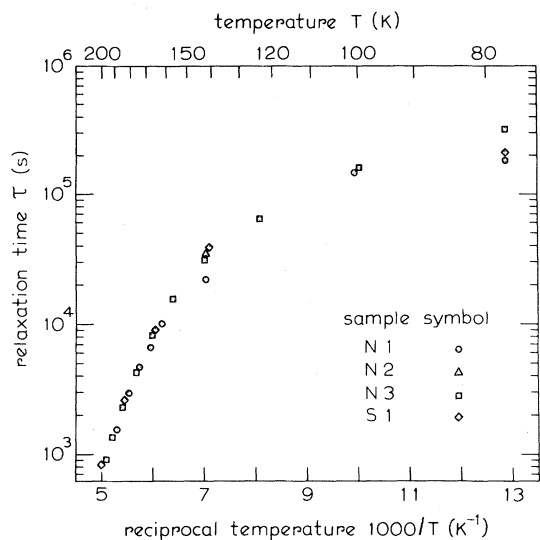


FIG. 1. The reorientation time constant τ for anneal of stress-induced ordering of substitutional nitrogen in diamond as a function of anneal temperature, as obtained from the static experiments in the low-temperature region.

viously reported high-temperature reorientation studies.^{11,12} At high temperatures the rapid reorientation of centers was observed dynamically by its effect on EPR line widths and averaging of line positions. The high-temperature reorientation frequencies ν were fitted by an Arrhenius relationship

$$\nu = \nu_0 \exp[-V(0)/kT], \quad (1)$$

with $\nu_0 = 4 \times 10^{12} \text{ s}^{-1}$, $V(0) = 0.76 \text{ eV}$,¹¹ or $\nu_0 = 10^{13}$

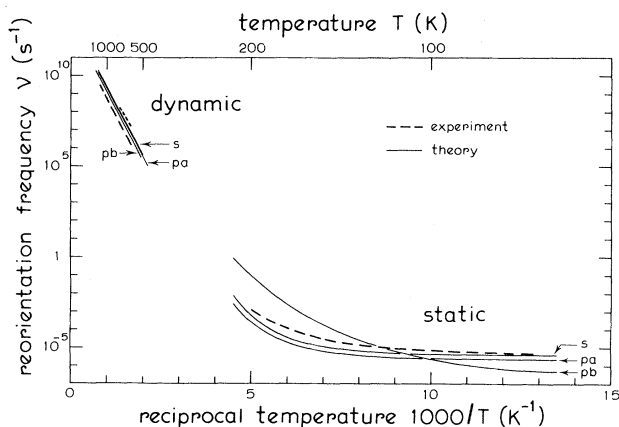


FIG. 2. Experimental reorientation frequencies (dashed lines), measured in the dynamic and static regimes, compared with calculated frequencies (solid lines) for barriers of sinusoidal (s) and parabolic type a (pa) and b (pb).

s^{-1} , $V(0) = 0.7 \text{ eV}$.¹² Reorientation frequencies reported for these dynamical experiments at high temperature are shown in Fig. 2. Also included are the present results obtained at low temperature where the reorientation process was observed under static conditions.

In the temperature range indicated by "static" in Fig. 2 the reorientation frequencies observed are very much higher than expected on the basis of an extrapolation of the high-temperature dynamic data. In order to explain these more rapid reorientations we consider the mechanism of tunneling. In a simple model we describe the motion of the nitrogen atom in a static potential created by the surrounding diamond crystal. In the treatment we include tunneling between excited vibrational states in the potential wells.¹³ On the basis of the one-dimensional quasiclassical (WKB) approximation the tunneling frequency $\nu_{i,n}$ is given by¹⁴

$$\nu_{i,n} = \frac{\nu_0}{\pi} \exp \left\{ \frac{-1}{\hbar} \int_{V(x) > W_n} [2m(V(x) - W_n)]^{1/2} dx \right\}, \quad (2)$$

with ν_0 the mode frequency, $V(0)$ the maximal barrier height at position $x = 0$, and m the reduced mass of vibration. The energy W_n of the n th excited vibrational state is equal to $W_n = (n + \frac{1}{2})\hbar\nu_0$, on the assumption that the potential well is parabolic near its bottom. The thermal occupancy f_n of level n is related to the occupancy f_0 of the ground state by

$$f_n = f_0 \exp[(W_0 - W_n)/kT] = f_0 \exp(-n\hbar\nu_0/kT), \quad (3)$$

and is normalized by $\sum_{n=0}^{\infty} f_n = 1$. The total reorientation frequency ν is obtained by a summation of the effective reorientation rates via ground and excited states. By solving rate equations for the transitions between the four potential minima one obtains

$$\nu = \sum_{n=0}^{\infty} 4f_n \nu_{i,n}. \quad (4)$$

The validity of this expression is restricted to low temperatures, when only the lower vibrational levels are occupied and the effects of anharmonicity can be neglected. At high temperatures the reorientations by thermally activated jumps over the potential barriers are governed by Eq. (1).

For actual calculations using this reorientation

model three different shapes of potential barrier were considered. Two of these are parabolic, labeled pa and pb , respectively; the third, labeled s , is sinusoidal. The parabolic barriers are characterized in Fig. 3; the sinusoidal barrier, not illustrated, is defined by $V(x) = V(0) \times \cos^2(\pi x/L)$. The mode frequency ν_0 , maximal barrier height $V(0)$, and barrier width L are related by

$$\pi^2 m \nu_0^2 L^2 = 4V(0) \quad (5a)$$

for barrier type pa , by

$$\pi^2 m \nu_0^2 L^2 = 2V(0) \quad (5b)$$

for barrier type pb , and by

$$2m\nu_0^2 L^2 = V(0) \quad (5c)$$

for barrier type s . If we assume values for ν_0 and $V(0)$ straightforward calculations of the reorientation frequencies can be made. For the parabolic barriers these calculations are entirely analytic; in the case of the sinusoidal barrier the integral in Eq. (2) has to be evaluated numerically. Results of such calculations are presented in Fig. 2 for comparison with the experimental data. The calculated curves as shown were obtained with a barrier height $V(0) = 0.76$ eV and mode frequency

$$\nu_0 = 1.4 \times 10^{13} \text{ s}^{-1} \quad (6a)$$

for barrier type pa ,

$$\nu_0 = 7.6 \times 10^{12} \text{ s}^{-1} \quad (6b)$$

for barrier type pb , and

$$\nu_0 = 1.58 \times 10^{13} \text{ s}^{-1} \quad (6c)$$

for barrier type s . A satisfactory match is obtained for the potentials pa and s , though these potentials predict too small a temperature de-

pendence at the lowest temperatures. As a result of the smaller interlevel distance the temperature dependence in this region is too pronounced for potential pb . A best general agreement with the experimental data is given for a potential of type pa or s , with possibly a slight distortion of the bottom of the well towards pb . In the calculations phonon-assisted tunneling was not taken into account. We conclude that the reorientation rate in the temperature range $78 < T < 200$ K can be explained in a natural way by tunneling between ground states and higher vibrational states which are populated by thermal activation. The same two parameters ν_0 and $V(0)$ which describe the high-temperature reorientations are also applicable in the tunneling regime.

The oscillation frequencies (6a) and (6c) correspond to a wavelength $\lambda \approx 20 \mu\text{m}$. This may be compared with the measured vibrational absorptions associated with nitrogen in diamond, which fall in the $7\text{--}10\text{-}\mu\text{m}$ band.¹⁵ The discrepancy is possibly related to the use of a simplified model in which the lattice surrounding the nitrogen atom does not distort. In this model the barrier width L can be estimated by use of the relations (5a) and (5c). We obtain, with the parameters in (6a) and (6c) and taking for m the nitrogen mass, $L = 0.103$ nm. On reorienting from one $\langle 111 \rangle$ distorted site to another the nitrogen atom may move on the circumference of a circle, which has its center on the regular lattice position, over the tetrahedral angle. From the length L of the arc the magnitude of the distortion Δd is estimated to be $\Delta d = 0.054$ nm. In relation to the nearest-neighbor distance of diamond, $d = 0.154$ nm, this amounts to 35% distortion. This is an unusually large effect. Previous values reported for the distortion are about 10% from hyperfine axes,^{5,7} 26% from extended Hückel theory,¹⁶ 5%

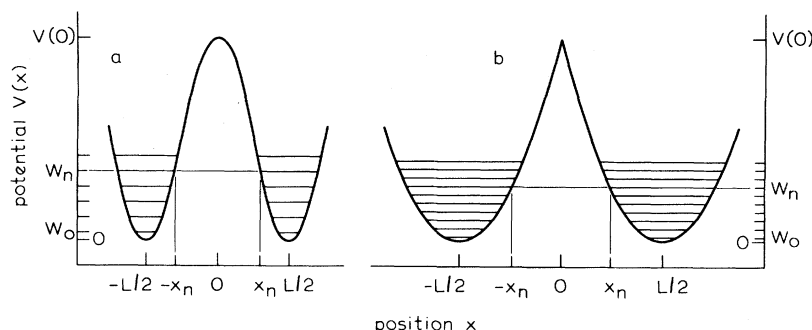


FIG. 3. The parabolic potential barriers considered in the analysis of the low-temperature reorientation frequencies.

from extended Hückel theory,¹⁷ (5 to 10)% from complete neglect of differential overlap,¹⁸ and up to 0.05 nm by Stoneham.²

Recently substitutional nitrogen in silicon was observed in EPR after implantation and laser annealing.¹⁹ The center, similar to nitrogen in diamond, is trigonally distorted. The reorientation frequency in the silicon case is reported to obey an Arrhenius relationship. The activation energy for reorientation, measured to be 0.084 eV, is considerably lower than the corresponding value in diamond. For tunneling between ground states of potential wells the approximate order of the tunneling rate is given by $\nu \approx (4\nu_0/\pi) \exp(-4S)$, with $S = V(0)/h\nu_0 \approx [2mV(0)]^{1/2}L/h$, using Eqs. (2), (5a), and (5c). The barrier height $V(0)$, which is larger for diamond, only enters through the square root. The barrier width L , which tends to be smaller for diamond because of its smaller lattice parameter, enters linearly. Apparently the latter factor dominates the final result.

In summary, we found for the reorientation rate of the distorted nitrogen center in diamond a strong deviation from Arrhenius-type behavior. At high temperatures reorientation is a thermally activated process, whereas at low temperatures the tunneling mechanism is rate determining. A mixed process of thermal activation and tunneling between excited states is active for intermediate temperatures. In a simple model, with a static potential well, the displacement of the nitrogen atom is estimated.

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