21. THE JAHN-TELLER EFFECT OF NITROGEN IN DIAMOND

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The isolated substitutional nitrogen centre, as it occurs in type Ib diamond, spontaneously distorts from cubic to trigonal symmetry because of the Jahn-Teller instability. As a consequence of this lower symmetry four different orientations in the diamond lattice are available to each nitrogen centre. Alignment of the centres can be induced by subjecting the crystal to uniaxial stress. This stress-induced ordering can be monitored using electron paramagnetic resonance [(1)].

In previous studies reorientations of nitrogen in diamond were observed at temperatures between 600 and 1200 K [(2,3)]. In this temperature region the process of reorientation is by thermally activated jumps over the potential barriers separating the different orientations. The results for the time constant τ were described by the Arrhenius expression $\tau = \tau_o \exp(E/kT)$, with $\tau_o = 2.5 \times 10^{-13}$ s and barrier height E = 0.76 eV [(2)]. The present experiments on reorientations of nitrogen were carried out on three natural type Ib diamonds in the temperature interval 77 K < T < 197 K. The time constants τ found at these low temperatures were many orders of magnitude smaller than expected from extrapolation of the high temperature results. Also, at low temperatures, the slope of the τ versus T^{-1} curve is smaller, indicating a lower activation energy. These observations imply that for reorientations at low temperatures the process of quantummechanical tunneling is involved. With the values for τ_o and E as given above, and using the concept of tunneling between excited states, the present results can be explained satisfactorily.

The time constants for inducement of ordering with external stress applied were found to be equal to the time constants for anneal of alignment with the stress removed. Introductory experiments showed that ionizing the nitrogen donors by illumination strongly enhances the erasion of stress-induced ordering at low temperatures.

To first approximation the Jahn-Teller effect, of a T_2 electronic state coupled to a trigonal τ_2 distortion mode, is described by the perturbation Hamiltonian

$$\mathcal{H}_{JT} = B\begin{pmatrix} 0 & Q_6 & Q_5 \\ Q_6 & 0 & Q_4 \\ Q_5 & Q_4 & 0 \end{pmatrix} + \beta(Q_4^2 + Q_5^2 + Q_6^2)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The collective coordinates for the distortion are Q_4, Q_5, and Q_6, while B and $\beta = m\omega_0^2/2 = 2\pi^2 m/\tau_0^2$ are the coupling constants. By solving the perturbation problem equal minimum values for the energy are found for four distortions which satisfy $|Q_4| = |Q_5| = |Q_6| = 2B/3\beta$. The Jahn-Teller stabilisation energy in these minima is given by $E_{JT} = 2B^2/3\beta$, and the height of the reorientation barriers is $E = B^2/6\beta$. With the experimental data for τ_0 and E one calculates $B \approx 10^{-8}$ J/m and $\beta \approx 10^2$ J/m^2. This corresponds to a static distortion $|Q_4^0| = |Q_5^0| = |Q_6^0| = 0.67 \times 10^{-10}$ m.

References

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