

radiation. It is interesting to note that to obtain a photographic density I in the investigated films at these intensities it is necessary to use exposure times longer than 10^4 sec¹).

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ELECTRON PARAMAGNETIC RESONANCE OF NICKEL IN SYNTHETIC DIAMOND

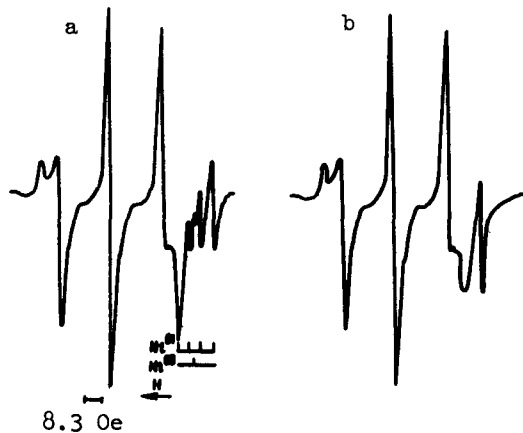
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Synthetic diamonds obtained in nickel-containing systems exhibit at $T < 150^\circ\text{K}$ an isotropic ($g = 2.032 \pm 0.001$) electron paramagnetic resonance (EPR) spectrum from one line (in addition to the triplet due to the disperse paramagnetic nitrogen [1]). Two hypotheses were advanced earlier [2 - 4] concerning the nature of this line. Loubser and Ryneveld [2], and we [3, 4] proposed that the observed spectrum is due to nickel Ni^{1+} with configuration $3d^9$ and effective spin $S = 1/2$, or to Ni^{1-} with configuration $3d^8$ and a bound hole in the valence shell, similar to nickel in germanium [5], with the same effective spin $S = 1/2$. Bratashevskii et al. [6] connected the given line with the interstitial carbon atom (a system with $S = 1$ and $L = 1$ is not a "good" quantum number, owing to the weak spin-orbit coupling).

We have already written [4] that the anisotropy of the spectrum is evidence of a manifestation of the Jahn-Teller effect, similar to that occurring for the EPR spectrum of nickel in germanium [5]. In diamond, however, unlike in germanium, where an anisotropy of the g -tensor is observed already at $T \leq 20.4^\circ\text{K}$, the spectrum remains almost isotropic down to $T = 4.2^\circ\text{K}$. Introduction of donor impurities (phosphorus, nitrogen) into diamond, other conditions being equal, leads to a decrease of the intensity of the EPR lines of nickel. This is connected with the fact that the latter form two acceptor levels, so that the intensity of the EPR signal is directly proportional to the filling of the lower level and inversely proportional to the filling of the upper level [4, 5].

However, all the data presented so far on the nature of the isotropic line $g = 2.032$ in diamond were indirect [1 - 4], since the content of the Ni^{61} isotope in natural compounds is 1.2%. We therefore have grown, by the usual

¹)The significance of the results to the theory of the sensitization of the photographic process and physical simulation of the main photosynthesis reaction - the photolysis of water - will be discussed elsewhere.



method, diamond crystals in a system containing the isotope Ni^{61} (enrichment 86%). The EPR spectrum of the obtained crystals (all the measurements were performed on powdered samples at $T = 77^\circ\text{K}$) is shown in the figure, which gives, for comparison, also the EPR spectrum of ordinary diamonds.

As is well known, the nuclear spin of the isotope Ni^{61} is $I = 3/2$, and therefore the appearance of an isotropic hyperfine structure (hfs) of four lines (the weak central line is due to the isotope Ni^{60} , and the fourth hfs line is superimposed on the side component of the EPR spectrum of the donor

nitrogen [1]), points to a connection between the observed EPR spectrum and the nickel impurity. The magnitude of the hfs is 6.5 ± 0.5 Oe, and the g factor is 2.032 ± 0.001 . It can be assumed that the appearance of a very weak additional doublet structure $A = 2.7$ Oe, reported in [6], is due to the interaction of the unpaired spin with the nucleus of the isotope C^{13} ($I = 1/2$, content 1.1%). The presence of only one pair of lines is due to a shift of the nickel to one (or two) of the four surrounding carbon atoms as a result of the presence of the Jahn-Teller effect.

The fact that the observed lines of the EPR spectrum have a small half-width (~ 2 Oe at the inflection points) and broaden greatly with increasing temperature (the spectrum is practically unobservable at $T > 150^\circ\text{K}$) is evidence of the strong temperature dependence of the Jahn-Teller reorientation frequency. Two types of reorientation are possible: inversion and shift along any of the six directions corresponding to the three edges of the cube (four-fold mirror-rotation axes in a regular tetrahedron). It can be assumed that the tetrahedron surrounding the nickel atom is somewhat distorted, as a result of one or two carbon atoms, and the dynamic Jahn-Teller effect, which undoubtedly also takes place, leads to additional [7] distortions (reorientations). Attention should be called to the different intensities and half-widths of the EPR lines of the quartet structure, this being connected with the fact that certain types of reorientation do not change the g-factor and the line will broaden at different rates on going from low temperatures to higher ones.

The lack of large single-crystal samples enriched with Ni^{61} does not make it possible to investigate the properties of the anisotropic EPR spectrum at low temperatures, when "freezing" of the spectrum should take place. This does not make it possible to determine the electron configuration of the nickel in the diamond.

Thus, nickel is an experimentally identified structure impurity (the second next to nitrogen) in diamond.

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OPTICAL ORIENTATION OF ELECTRON SPINS AND BAND SPLITTING IN DOPED SEMICONDUCTORS

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The optical orientation of the electron spins in interband absorption of circularly-polarized light in semiconductors can be used to study a number of characteristics of band splitting. The experimental results presented below illustrate the possibilities of this method for the study of the shift of the split-off valence band in doped p-GaAs, and also for the investigation of the splitting of the conduction band. This splitting, which occurs in crystals without an inversion center, should lead to additional spin relaxation. As shown by D'yakonov and Perel' [1], its rate increases rapidly with the energy of the electrons in the conduction band. At an energy E_{hv} of the exciting-light quanta, satisfying the condition $E_{hv} - E_g \ll \Delta$ (E_g is the width of the forbidden band, and Δ is the spin-orbit splitting of the valence band), the spin orientation is maximal. In this case the spin relaxation corresponds to relaxation of the thermalized electrons and is characterized by a time τ^{ST} . With increasing $E_{hv} - E_g$, the additional relaxation due to the splitting of the conduction band can lead to a change in the type of the observed dependence of the degree ρ of the circular polarization of the recombination radiation on E_{hv} , to the extent even that the sign of the polarization may reverse.

It was found in [2] that there is a systematic discrepancy between the theoretical and experimental plots, $\rho_T(e_{hv})$ and $\rho_e(E_{hv})$, for p-GaAs with concentration $2 \times 10^{19} \text{ cm}^{-3}$. It was shown in [3], however, that this discrepancy is due to the different values of τ^{ST} in the interior and on the surface of the sample. The results of [3] led to the conclusion that the spin orientation is conserved during energy and momentum relaxation of the conduction electrons in the case of a strongly-doped semiconductor. As shown in [1], scattering by impurities decreases the influence of the conduction band splitting on the spin relaxation (an effect analogous to the narrowing of the paramagnetic-resonance lines in liquids and gases). Therefore an investigation of the effective spin relaxation of non-thermalized electrons should be carried out either at lower impurity concentrations than in [2], or else at high energies.

Figure 1 shows a plot of $\rho(E_{hv})$ for an impurity concentration $3 \times 10^{18} \text{ cm}^{-3}$ in the energy interval $E_g \lesssim E_{hv} \lesssim E_g + 3\Delta$ at 77°K. The line width of the exciting light at the base was $\sim 20 \text{ MeV}$. To exclude the analyzer errors in the measurement of the weak circular-polarization signals (U_σ), the excitation was carried out both with right (σ^+) and left (σ^-) circularly polarized light. The values of $\rho(E_{hv})$ shown in Fig. 1 were obtained from the values of $(U_{\sigma^+} + U_{\sigma^-})/2$. At $E_{hv} \approx 2.02 \text{ eV}$, the sign of the circular polarization reversed. A reliable criterion for the observation of the spin orientation with the aid of recombination radiation is the depolarization of this radiation in a magnetic field H . The plots of $\rho(H)$ shown in Fig. 2 were also calculated from the values of $(U_{\sigma^+} + U_{\sigma^-})/2$ at different H for three values of the wavelengths. Observation of the depolarization of the recombination radiation in