

NICKEL STRUCTURAL IMPURITIES IN NATURAL DIAMONDS

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Since 1950s much attention of researchers has been directed to structural impurities of nitrogen in natural diamonds (Field, ed., 1992). It has been shown by modern methods that nitrogen forms several different defects that can modify physical properties of diamonds. Structural impurities of nickel have been investigated in synthetic crystals grown from nickel-containing melts.

In the course of study of a collection including about 100 crystals of 1-2 carats in weight from Yakutia and Ural deposits (Russia) we revealed structural impurities of nickel in natural diamonds by EPR (electron paramagnetic resonance). In this report the types of nickel paramagnetic centers and the distribution of nickel impurities within a diamond crystal will be considered.

Samples and methods. Nickel structural impurities were detected in 17 among 19 yellow stones from our collection. Most diamonds were commonly occurring octahedra with parallel or shear-form lines on the edges and negative trigons on the faces. Three stones were rounded dodecahedra. Two diamonds had a cubic habit. According to physical classification, nickel-containing diamonds fall under types Ia and Ia+Ib, as their IR-spectra indicate.

The EPR-spectra were recorded with Varian E-115 and RE-1306 spectrometers in X band (about 9 GHz) with modulation frequencies of 100 and 25 kHz at temperatures of 77 and 293 K.

To determine of the distribution of nickel impurities, the plate was cut through the center of the sample where the maximum concentration of nickel paramagnetic centers was recorded. The plate was studied by ion microprobe analysis at Institute of Crystallochemistry and Crystallography of CNR in Pavia (Italy), by X-ray diffraction topography with C.G.K camera, by cathodoluminescence topography in SEM "Stereoscan MK-IIA" with a color display of video information and by local cathodoluminescence spectroscopy using the "Electron Gun" pulse beam with the electron energy of 40 keV.

Nickel paramagnetic centers. Analysis of EPR-spectra shows that nickel is included into the natural diamond structure as the ion Ni^{+} forming the NE1, NE2, and M1 paramagnetic centers.

The paramagnetic centers NE1 and NE2 were originally found in synthetic treated diamonds grown in the Fe-Ni-C system (Nadolinny and Yelissev, 1993). These centers give rise to a complicated system of EPR lines having the anisotropic g-factor ranging from 2.007 to 2.130. It has been proposed that the center NE1 is a double semivacancy with the Ni⁺ ion at the center and with two nitrogen atoms located in the first coordination sphere (Nadolinny et al., 1997). The nitrogen-nickel-nitrogen direction makes 14° with the [110] direction of diamond lattice. The NE2 center is similar to the NE1 one, joining an additional nitrogen atom.

The M1 centers (Mineeva et al., 1994) first indentified during the study of our diamond collection have been observed as single lines with the widht of 3×10^{-4} T, with each center having 6 geometrically nonequivalent positions. The center has a tetragonal symmetry and $S=1/2$ together with $g_{\parallel} = 2.0151$, $g_{\perp} = 2.2113$. This center appears to be a donor-acceptor pair in which an acceptor (possibly B or Al) substitutes C and a donor ion Ni⁺ is situated in the nearest interstitial position.

The maximum concentration of the centers NE1 and NE2 in studied diamonds reached the value $1.6 \times 10^{18} \text{ cm}^{-3}$ and that of M1 centers reached the value $1.0 \times 10^{17} \text{ cm}^{-3}$. But in most crystals the concentrations of nickel centers exceeded the detection limit of the EPR-spectrometer (above 10^{16} cm^{-3}) only marginally. Among the 17 crystals with NE1 and NE2 centers, only in 4 samples the M1 centers were revealed.

In synthetic diamonds grown in nickel-containing systems the paramagnetic centers Ni_s⁻ which representing a single Ni ion in a substituted position are quite common. After annealing at 2150 K and 55 kbar the simple Ni_s⁻ centers are transformed into more complex centers NE1 and NE2 (Nadolinny et al., 1997) which have just been detected in natural diamonds.

As it is known, a similar tendency was established for the most abundant nitrogen impurities in diamonds. Synthetic diamonds contain nitrogen as single substituting atoms. After experimental heating single nitrogen atoms are transformed to more aggregate A-, B1-, B2- defects (Field, ed., 1992). In natural crystals these aggregate defects occur most oftenly.

Distribution of nickel impurities within a crystal. X-ray diffraction topographs of the diamond with the maximum concentration of nickel centers indicated that this crystal had a complicated growth history. During the first growth stage only cubic sectors grew. After cubic and octahedral sectors developed simultaneously. Finally, cubic sectors grew out and the crystal joined octahedral morphology.

Ion point-by-point microprobe analysis through the (001) growth sector confirmed the presence of nickel impurities in the crystal and revealed their non-uniform distribution (though this technique discloses all types of nickel impurities, not only the structural ones). The first growth

band systems of the sector did not involved nickel impurities and exhibited blue cathodoluminescence emission. The following 2-4 bands contained nickel and emitted red light. In the area, where (001) sector grew out, these impurities were not observed and the emission was blue also. In the (00 $\bar{1}$) sector the same distribution of luminescent colors was observed. Cathodoluminescence of all octahedral growth sectors was blue.

In cathodoluminescence spectra the broad band with a peak near 920 nm (1.35 eV) was detected in all growth bands of the (001) sector. But two sharp zero-phonon lines at 788 and 793 nm (1.573 and 1.563 eV, respectively) were found in the nickel-containing bands only.

On the basis of the spatial correlation it is possible to suggest that the red emission seen in cathodoluminescence topographs and lines at 788 and 793 nm in cathodoluminescence spectra are due to the presence of nickel impurities. Since the area with red emission occupied about 50% of the studied crystal volume, it might be supposed that the actual concentration of nickel centers is at least twice the above mentioned value, that was calculated from the net volume of the crystal.

Conclusions. Thus, structural impurities of nickel in natural diamonds, as well as nitrogen ones, are non uniformly distributed through the crystal volume and form complex centers, which may arise as a result of high temperature annealing. These data seem to indicate that natural diamonds grew under varying conditions and were subjected to heating under high T-P parameters, which appears to be characteristic for the Upper Mantle.

References

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