ABSORPTION SPECTRA OF DIAMONDS OF INTERMEDIATE TYPE

CRYSTALLOGRAPHY

1969

SovietRxiv

Abstract

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UDC 549.211

CRYSTALLOGRAPHY

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ABSORPTION SPECTRA OF DIAMONDS OF INTERMEDIATE TYPE

(Presented by Academician N. V. Belov on 29 IV 1969)

On the basis of the features of the absorption spectra in the infrared and ultraviolet regions of the spectrum, natural diamonds are divided into two types (^{1}). Kaiser and Bond (^{2}) found in type I diamonds a significant amount of nitrogen (up to $4 \cdot 10^{20}$ atoms/cm^3) and established a direct correlation between the nitrogen content in the crystal and the intensity of the absorption band at 1282 cm^{-1}, which was recently confirmed by Lightowlers (^{3}) with the aid of activation analysis. Depending on the forms of distribution of nitrogen in the crystal lattice, type I diamonds are subdivided into groups Ia and Ib (^{4}). Type II diamonds contain practically no nitrogen.

More detailed studies made it possible to detect diamond crystals with a reduced nitrogen content of 10^{18}–10^{19} atoms/cm^3. On the assumption that they are a genetically transitional group of diamonds between types I and II, they came to be classified as diamonds of intermediate type (^{5}, ^{6}).

The physical properties of diamonds of intermediate type have not been studied sufficiently fully. In this connection, the present work sets forth the results of investigations of the infrared and ultraviolet absorption spectra of 82 diamond crystals of intermediate type, undertaken in order to clarify the spectral features as a function of the concentration of nitrogen in them as an impurity.

The diamond crystals consisted of distorted octahedra, fragments, and twins 0.9-3 mm thick. The number of regular octahedra amounted to 5% of the total number of diamonds. All the specimens were colorless and transparent, with fairly strongly developed growth traces.

According to the form of their spectra in the region of one-phonon absorption (1400-1000 cm^{-1}), the specimens studied are subdivided into 5 groups (Fig. 1). The maxima of most of the distinct bands coincide within $\pm 3 cm^{-1}$ with the observations of other authors.

The first group included diamonds that had no absorption bands in this region (Fig. 1A). The number of these nitrogen-free diamonds, belonging to type IIa, amounts to 6% of the total number of crystals. The limiting sensitivity of our instrument to nitrogen, determined as in work (^{2}), is estimated as 10^{17} atoms/cm^3.

The second group comprises 18% of the diamonds studied. In their spectra the crystals of this group are ordinary type Ia diamonds (Fig. 1B), but with a lower nitrogen concentration. For different crystals the concentration ranged from $1.1 \cdot 10^{18}$ to $2.4 \cdot 10^{19}$ atoms/cm^3. In this group it was noted that, with an increase in the intensity of the 1370 cm^{-1} band, the 1282 cm^{-1} band increased in approximately the same ratio.

The third group of diamonds is comparatively rare (8%). In the spectra of these crystals (Fig. 1V) the intensity of the bands at 1335, 1175, and 1010 cm^{-1} increases in comparison with the spectrum of diamonds of the preceding group. The nitrogen content, according to our measurements, varied within the limits $2 \cdot 10^{18}$–$2.5 \cdot 10^{19}$ atoms/cm^3, i.e., approximately the same as in the second group.

The fourth group comprised 17% of the specimens. In the spectra of the corresponding crystals the intensity of the bands at 1335, 1175, and 1010 cm^{-1} is still greater

increases, while the 1282 cm^{-1} band decreases (Fig. 1). The 1370 cm^{-1} band was not observed in all specimens. The nitrogen content increased to $1.8 \cdot 10^{19}$ $-4.4 \cdot 10^{19}$ atoms/cm^3.

The fifth group was the most representative; it included 51% of the crystals. The spectra are characterized by the complete disappearance of the 1282 and 1370 cm^{-1} bands and a further strengthening of the 1335, 1175, and 1010 cm^{-1} bands (Fig. 1). The nitrogen concentration varies from 10^{19} to more than 10^{20} atoms/cm^3 in individual crystals. In terms of the amount of nitrogen in them, such specimens could be assigned to type Ia diamonds, but the shapes of their spectra differ substantially from the spectra of the latter.

In all the spectra of the crystals without exception, the 1135 cm^{-1} band, attributed to dispersed nitrogen (4), was not found. This was confirmed by the absence of EPR signals in the region $g \simeq 2.0$, checked for a number of specimens on an -2 spectrometer at room temperature.

The edge of intrinsic absorption in the UV region of the spectrum for diamonds of all five groups shifted from 225 to 246 mµ, depending on the concentration of impurity nitrogen (Fig. 2). Absorption lines at 230.2 and 231 (doublet); 235.9 and 236.2 (doublet) 240; 246 and 249 mµ were also observed in the spectra, previously mentioned in connection with diamonds of intermediate type (7, 8).

According to current views, the 1370 and 1282 cm^{-1} bands are due to vibrations of the diamond crystal lattice perturbed by local aggregated formations of impurity nitrogen. The first of the bands, as shown in (9), is connected with lamellar nitrogen inclusions in the form of the well-known "platelets" (10). The 1282 cm^{-1} band is due to associations in the form of groups of neighboring

Fig. 1. IR spectra of diamonds in the region of single-phonon absorption (Leitz IIIG spectrophotometer with microattachment 6:1, NaCl prism)

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Fig. 2. UV absorption spectra of diamonds (DFS-8m spectrograph with WHS-20 hydrogen lamp): 1 –diamonds of the first group; 2 –second-third group; 3 –third-fourth group; 4 –fourth-fifth group

Figure 2: Fig. 2. UV absorption spectra of diamonds (DFS-8m spectrograph with WHS-20 hydrogen lamp): 1 –diamonds of the first group; 2 –second-third group; 3 –third-fourth group; 4 –fourth-fifth group

Fig. 1. IR spectra of diamonds in the region of single-phonon absorption (Leitz IIIG spectrophotometer with microattachment 6:1, NaCl prism)

nitrogen atoms N—N (11). The interpretation of the remaining bands 1335, 1175, 1100, and 1010 cm^{-1}, assigned to the B-system of bands according to (12), is still not clear.

Until now, diamonds of intermediate type had been assigned (11) a spectral form similar to the spectra of diamonds of the fifth group (Fig. 1). The data we obtained on IR spectra showed that there exists an ···

there are several groups of diamonds among diamonds of intermediate type; of these, the first and second groups belong to the known types of diamonds (types IIa and Ia, respectively). The third group is distinguished by a characteristic spectrum. The fourth group is transitional between the third and fifth groups. It may be asserted that if in crystals of the second group nitrogen is present in the form of two known forms–platelets and N–N–then in the fifth group these forms of nitrogen distribution in the diamond crystal lattice disappear or are substantially reduced. The considerable nitrogen content, the large number of diamond samples of the fifth group, and the specificity of their spectra are undoubtedly due to another nature of impurity-nitrogen inclusions, possibly in combination with other lattice defects. It is entirely justified to distinguish crystals of the fifth group as a new subtype of diamond classification, for which the name “intermediate,” indicating a low nitrogen concentration in the crystals, is not entirely suitable.

It is interesting to note that in the groups of intermediate diamonds nitrogen is distributed differently. For example, in diamonds of the second group nitrogen is distributed comparatively uniformly throughout the entire volume of the crystal. In diamonds of the third and fourth groups, aggregated nitrogen is located mainly in the surface layers of the crystal faces in the (111) plane. These results were obtained by successively measuring the intensities of the corresponding IR bands in the spectrum of a crystal after several grindings along its end faces.

Fig. 2. UV absorption spectra of diamonds (DFS-8m spectrograph with WHS-20 hydrogen lamp):
1 –diamonds of the first group; 2 –second-third group; 3 –third-fourth group; 4 –fourth-fifth group.

The study of the UV absorption spectra of the samples showed that division of intermediate diamonds into groups according to their spectra in this region is impossible, since the intensity of the bands of the B-system, increasing with increasing ordinal number of the group, correlates only weakly with the position of the absorption edge of diamonds. At the same time, the total amount of nitrogen in the crystals is related to the position of the absorption edge with a correlation coefficient of only $r = 0.72 \pm 0.07$. This once again emphasizes the fact that the groups of intermediate diamonds are determined by the form of nitrogen distribution in the crystals, and not by the concentration of the latter in them.

In conclusion, we express our gratitude to B. V. Osipov and S. D. Zvonkov, who took part in the experiments.

Received
24 IV 1969

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