

ON A POSSIBLE ORIGIN OF THE ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF NITROGEN IONS IN DIAMOND

1969

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196901.37361>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

UDC 538.113

PHYSICS

V. N. LAZUKIN, A. N. TERENT' EVSKII

ON A POSSIBLE ORIGIN OF THE ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF NITROGEN IONS IN DIAMOND

(Presented by Academician L. A. Artsimovich, January 24, 1969)

Electron paramagnetic resonance (EPR) has been studied by a number of authors both in natural (¹⁻⁷) and in synthetic (^{8,9}) diamonds.

In a thorough work (¹), the EPR spectrum of the ion N^{4+} was investigated; at a definite position of the crystal relative to the constant magnetic field it consisted of three lines of equal intensity; at other orientations of the crystal both outer lines split into several components of equal intensity. Weak lines were also observed (with intensities approximately 200 times smaller than the principal ones), whose appearance the authors explained by the presence of an unpaired electron in the carbon-nitrogen ($^{13}C-^{14}N$) bond. The same point of view was later expressed in other works (^{2,3}).

Doubts concerning the validity of this hypothesis led us to undertake experiments aimed at a comprehensive examination of the EPR spectrum of natural diamond at a frequency of 9200 MHz. For the experiments a highly perfect crystal of South African origin was chosen, having the shape of a regular cube with an edge of about 5 mm and a faint lemon-yellow coloration.*

In the course of the experiments, special attention was paid to the study of the angular dependences of the lines of the EPR spectra, which made it possible to obtain more complete data and to formulate conclusions concerning the origin of some spectral lines different from those previously known.

It is known that in diamond the nitrogen ion can be located only at the center of a tetrahedron formed by carbon ions; four such tetrahedra make up the cubic cell in such a way that their vertices coincide with the vertices of the cube. The straight line connecting the carbon ion at the vertex of the cube with the nitrogen ion at the center of each tetrahedron determines the axis of anisotropy of the hyperfine splitting of the EPR spectrum. This means that if the angle θ between the constant magnetic field and the indicated axis is equal to 0° , then the EPR spectrum of the ion N^{4+} will be characterized by the value of the

Fig. 1

Figure 1: Fig. 1

hyperfine-splitting constant $A_{\parallel}$; but if $\theta = 90^\circ$, then this constant assumes the value $A_{\perp}$.

Leaving aside for the moment certain features of the EPR spectrum of the diamond under study (such as lines of impurity ions of the aluminum type or forbidden lines (Fig. 1, spectra 6, 7) of the nitrogen spectrum), let us consider the results of observations of the structure of the spectrum of the ion N^{4+} . Figure 1 presents the angular dependences of the lines of five varieties of this spectrum, described with high accuracy by the spin Hamiltonian ⁽¹⁰⁾:

$$H_{Mm_I} = H_0 - Km_I - \frac{K^2}{2H_0} [I(I+1) - m_I^2] + \frac{K^2}{2H_0} [S(S+1) - m_I(2M-1)], \quad (1)$$

* The authors express their gratitude to Yu. L. Orlov for the opportunity given them to study the described diamond and for the communication of valuable data on its physical properties, as well as the results of investigations of the chemical composition of related specimens.

where all the notation is conventional, and for the constant K the relation holds that is usual for hyperfine splitting:

$$K^2 = (A_{\parallel}^2 - A_{\perp}^2) \cos^2 \alpha \cos^2 \theta + A_{\perp}^2, \quad (2)$$

$\alpha = 54.5^\circ$.

The lines in the accompanying figure correspond to such a rotation of the crystal in the field H_0 for which a pairwise coincidence of the anisotropy axes of the hyperfine splitting for any values of θ is characteristic; this explains the splitting of the side lines of the spectrum of N^{4+} into two components, and not into four, as should be the case in general.

Curves 1 in the figure depict the behavior of a very intense "main" spectrum of N^{4+} : at $\theta = 0^\circ$ it consists of three lines of equal intensity,

Fig. 1. Angular dependence of the EPR lines of the N^{4+} ion in the diamond lattice. The EPR spectrum is symmetric with respect to the central line of the nitrogen ion, which does not shift in the field H upon rotation of the crystal (an axis of the angles θ is drawn from the point of the field H where this line is located). Owing to the indicated symmetry, the numbers are placed only in the left part of the figure, but nevertheless the central line and the

corresponding lines from the right half of the figure should be assigned to the spectrum designated by any given number.

of which the central one does not change its position and intensity when the angle θ changes, while both outer ones at the same time exhibit splitting into two components of half intensity. The intensity of lines 2, 3, 5 is approximately 200 times smaller than the intensity of the lines of the “main” spectrum; the authors of the cited works explain them by the presence of unpaired electrons in a carbon-nitrogen bond. From the curves it is evident that the directions of the anisotropy axes coincide for four spectra, 1, 2, 3, and 5. This means that if the hypothesis put forward in the cited works is correct, then the electron of the nitrogen ion interacts with at least four carbon ions located on one straight line. In this case one of these ions is located between the nitrogen ion and the carbon ion situated at the vertex of the tetrahedron, while the two others are located in neighboring cells. It is hardly possible to regard such a situation as physically justified.

It might have seemed possible to explain the appearance of spectra 2, 3, and 5 by the presence in the diamond lattice of impurity ions with nuclear spin $I = 1/2$, occupying the nitrogen site. However, in diamond there are no other suitable impurities besides $^{31}\text{P}_1$. But the spectrum of phosphorus in the present case consists of two lines (at

$\theta = 0^\circ$) or four lines (for $\theta \neq 0^\circ$ and 90°), which in fact is not observed (see Fig. 1). It seems more natural to assume that spectra 2, 3, and 5 owe their origin to the ion $^{14}\text{N}^{4+}$, differently bound to its surroundings. This is possible if, instead of a carbon tetrahedron, a tetrahedron of S^{4+} , Si^{4+} , and Se^{4+} is formed, at the center of which there is an N^{4+} ion. This assumption also explains the difference in the intensity of the “main” spectrum and spectra 2, 3, 5, since it is consistent with the data on the amount of impurities of the listed elements in diamond.

In summary, the following may be proposed. Spectra 1, 2, 3, and 5 owe their origin to the nitrogen ion $^{14}\text{N}^{4+}$ present in the tetrahedra of the elementary cell of diamond. In the first case the nitrogen ion is surrounded by 4 carbon ions; in the other three cases one of the ions of the carbon tetrahedron is replaced by one of the ions listed above. Apparently, in the case investigated the number of such possibilities is 3, i.e., there exist 3 types of bonds of the nitrogen ion with 3 different impurity ions in different tetrahedra or elementary cells. The spectra in all cases are identical, differing only in the magnitude of the splitting of the outer components. This is expressed in the difference between the hyperfine-splitting constants for the four spectra considered.

Spectrum 1	$A_{\parallel} = 40.8 \text{ Oe.}$	$A_{\perp} = 28.4 \text{ Oe.}$
» 2	$A_{\parallel} = 60.0 \text{ Oe.}$	$A_{\perp} = 17.0 \text{ Oe.}$
» 3	$A_{\parallel} = 99.0 \text{ Oe.}$	$A_{\perp} = 55.5 \text{ Oe.}$
» 5	$A_{\parallel} = 15.6 \text{ Oe.}$	$A_{\perp} = ?$
$g = 2.003$ for all these cases.		

A few words must be said about spectrum 4, which we have not touched upon until now. This spectrum belongs to the nitrogen isotope ^{15}N (nuclear spin $I = 1/2$). It has 2 lines of hyperfine structure, each of which is split into 2 components because of the nonequivalent positions of the $^{15}\text{N}^{4+}$ ion. The intensity of the lines of spectrum 4 is approximately 200 times less than that of the lines of spectrum 1. This agrees with the results of observations of the EPR spectrum of gaseous nitrogen ⁽¹¹⁾: the spectrum consisted of 3 lines belonging to ^{14}N , and 2 lines to ^{15}N . The ratio of the splitting constants for the two isotopes was equal to 1.39.

In our case $A_{15\parallel} = 56.5$; $A_{15\perp} = 39.6$, and the ratio $A_{15\parallel}/A_{14\parallel} = A_{15\perp}/A_{14\perp} = 1.39$ coincides with that found in ⁽¹¹⁾ with high accuracy for all values of the angle θ .

Moscow State University
named after M. V. Lomonosov

Received
6 I 1969

CITED LITERATURE

1. W. V. Smith, P. P. Sorokin et al., Phys. Rev., **115**, 1546 (1959).
2. W. V. Smith, G. J. Lasher, Brit. J. Appl. Phys., **16**, 475 (1965).
3. H. J. Bower, M. C. R. Simons, Nature, **210**, 1037 (1966).
4. E. A. Faulkner, P. W. Whippey, R. C. Newman, Phys. Mag., **12**, 413 (1965).
5. E. V. Sobolev, G. B. Bokii, ZhSKh, **5**, 557 (1967).
6. E. V. Sobolev, G. B. Bokii, N. D. Samsonenko, ZhSKh, **6**, 460 (1965).
7. N. D. Samsonenko, FTT, **6**, 3086 (1964).
8. M. J. A. Smith, B. R. Angel, Phil. Mag., **15**, 783 (1967).

9. S. M. Huggins, P. Cannon, *Nature*, **194**, 829 (1962).
10. V. N. Lazukin, A. N. Terent' evskii, *ZhETF*, **55**, 1612 (1968).
11. C. J. Ultee, *Chem. Phys.*, **43**, 1080 (1965).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.