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The structure of paramagnetic centres and the formation of defects in the B-C, B-C-Ti and B-C-Cr systems

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In this work a radiospectroscopic investigation of the B—C, B—C—Ti and B—C—Cr systems was made in the range of 0 to 30 at % carbon at 4.2, 77 and 300 K. It is shown that in the B—C system, with a change of carbon content from 0 to 30% there are two concentration ranges in which a change occurs in the character of EPR signal: the first from 0 to 13% carbon and the second where the carbon content is 18 to 30%. The g factor, the width, the form and the intensity of EPR lines indicate that in the first range the EPR signal is due to the $B_{12}C$ complexes, which represent the lattice of α-boron with one carbon atom. In the second range the experimental data indicate that probably the introduction of four carbon atoms occurs, so that the formation of $B_{12}C_4$ centres is in question. The change in intensity of the signal on introduction and increase of titanium and chromium contents indicates different mechanisms of interaction of the basic components in this system. Keeping in mind that with increasing content of addition the microhardness of samples increases, while the intensity of the EPR signal decreases, it is probable that larger amounts of the $B_{13}C_2$-phase, which is characterized by a higher microhardness, are then formed.

1. Introduction

The compounds of boron with carbon are very prospective semiconductor, high-temperature and abrasive materials. Their physical properties depend to a high degree on the stoichiometric ratio of components and the existence of definite additions, as well as on the technological conditions of preparation.

An integral consideration of the processes of formation of materials on the basis of boron and carbon is based on an analysis of the electronic and crystal structure of boron. Namely, an isolated boron atom in the ground state has an energetically unstable s^2p-electronic configuration, and on condensation in the solid state this causes transition to the not very stable sp^2 configuration, hence for the formation of the energetically most stable sp^3 configuration it tends to receive a free electron from donor atoms [1]. Depending upon technological conditions of preparation, elemental boron occurs in several forms: amorphous, α-rhombohedral, β-rhombohedral and tetragonal. X-ray investigations show that the crystal structure of boron represents, depending on form, differently connected icosahedra of the boron atom. Structural modifications of boron have a low degree of space replenishment; thus, for example, in the most stable β-boron this amounts to ~ 36%. The character of interatomic bonds in the boron structure and the existence of icosahedral voids are the basic causes of formation of interstitial solid solutions. Since α-rhombohedral boron and boron carbide ($B_{12}C_3$) are characterized by an identical arrangement of icosahedral polyhedra

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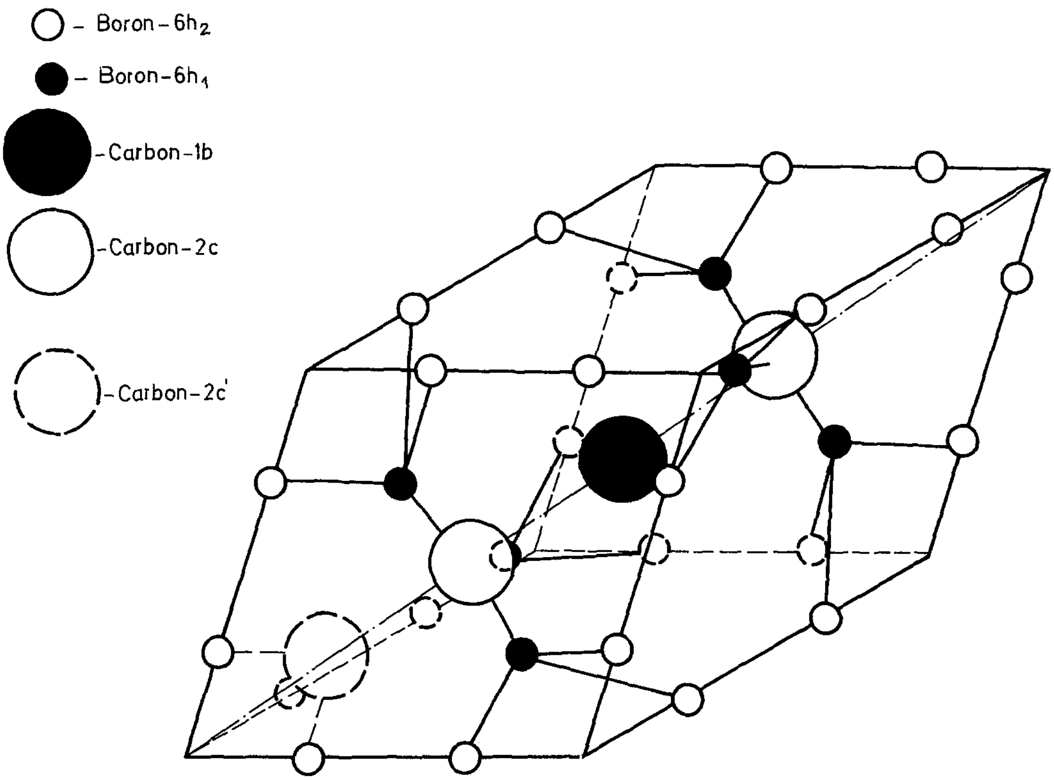

Figure 1 The elementary lattice of the boron–carbide.

[2], it is interesting to consider the process of carbide formation from the point of view of additional filling of icosahedral voids in α-boron by carbon atoms.

Fig. 1 shows the elementary lattice of $B_{12}C_3$, in which three carbon atoms are arranged along the diagonal of the rhombohedron (linear sequence C–C–C, sites 2c–1b–2c). It is assumed that four sp^3-orbitals of the carbon atom in the site 2c form three bonds with neighbouring boron atoms and one with the carbon atom which is in site 1b. In these atoms, which are in site 1b, there arise two σ-bonds with neighbouring carbon atoms because of the overlapping of sp- and sp^3-orbitals. The boron atom may also be in site 1b, and in this case boron carbide $B_{13}C_2$ is formed. Without participating in the formation of bonds, electrons of atom 1b pass to boron atoms in icosahedra.

With increasing carbon concentration, the process of interstitial solid solution formation should be characterized by a gradual filling of "vacant" sites of carbons on the diagonal of the rhombohedron and, owing to this, by the formation of atoms with uncompensated bonds. The existence of boron–carbon complexes with unconjugated bonds makes it possible to use electronic paramagnetic resonance for the study of the process of formation of the structure of B–C in a wide concentration range of components. Thus, for example, signal EPR registered in β-rhombohedral boron obtained by zonic melting, alloyed with carbon, was ascribed to an almost localized electron whose degree of localization depended on temperature [3]. The correlation between the concentration of spin centres and electrical conductivity of boron–carbide samples was investigated by Geist *et al.* [4], whereas Koulmann *et al.* [5] ascribe the resonance absorption line to the lattice of $B_{13}C_2$. The paramagnetism of the $B_{12}C_3$ system on a change of about 5% in the concentration of the components was also treated [6].

The absence of EPR data on a change in the properties of the B–C system over a wide range of concentrations of the components and the lack of a unified concept on the nature of paramagnetic centres arising during lattice rearrangement, stimulated our investigations of the B–C, B–C–Ti and B–C–Cr systems in the range 0 to 30 at % carbon.

TABLE I The chemical composition, EPR signal intensity and microhardness of the samples in the B–C–Me system

Additives	Temperature (° C)	Content of the component (wt %)			I (rel. unit)	ΔH (0e)	Microhardness (kg mm^{-2})
		B	C	Me			
Ti	1900	77.1	21.9	0.15	100	7	6190 ± 180
		75.8	21.2	1.4	98		6300 ± 220
		75.4	21.2	2.6	90		6400 ± 250
		73.6	21.0	4.9	60		7000 ± 350
		71.8	20.8	6.6	10		6200 ± 240
		67.2	21.3	11.0	2		
Cr	1500	72.2	18.3	9.0	2	7	3400 ± 250
	1520	73.5	19.2	6.3	10		4050 ± 220
	1530	74.1	20.8	4.7	25		4850 ± 380
	1540	75.2	21.0	2.9	30		5100 ± 400
	1570	77.0	26.6	1.1	37		3690 ± 260
	1600	77.4	21.1	0.11	40		4430 ± 350

2. Experimental details

The samples used in the experiments were obtained by mixing, pressing and heating in a vacuum of 10^{-3} mm Hg at a temperature of 1350° C for 1 h (samples no. 1) a corresponding quantity of amorphous boron, 99.8% pure, and lamp black containing ~ 0.2% ash. The samples were then ground into ~ 50 μm particles, mixed with a plasticizer (a 1 to 2% solution of rubber in petrol) and then pressed. The pellets were then sintered in vacuum at $T = 2300°$ C for 2 h (samples no. 2). Samples no. 3 were obtained by a two-step sintering (grinding was performed between the two sinterings) in a vacuum of 10^{-3} mm Hg at $T = 1800°$ C for 3 h. The B–C–Me (where Me is Ti, Cr) samples were sintered from elemental boron, lamp black and metals. Their quantity was determined taking into account the formation of $B_{12}C_3$ and MeB_2. Sintering was carried out in vacuum in the temperature range shown in Table I.

Radiospectroscopic investigation was made on a 3 cm PE 13-01 spectrometer at 300 and 77 K, and also on an 8 mm superheterodyne spectrometer at 300, 77 and 4.2 K.

3. Discussion of the results

3.1 EPR in the B–C–system

The registered EPR signal, in the 3 cm range, of powders with a particle size < 50 μm, indicates that we are dealing with an isotropic symmetric line with a g-factor of $g = 2.0025 \pm 0.0005$ whose width and integral intensity depends upon the concentration of carbon in the samples (Fig. 2). The shape of the line was almost Lorentzian. In some samples the decrease of line intensity at the ends indicates superposition of the given signal with a wider spectrum of smaller amplitude, but with the same g-factor. Measurements at 77 K did not detect a change in the position of the line, although its width somewhat decreased. Signal intensity in this temperature range obeys the Curie law. The maximum concentration of paramagnetic centres on the basis of EPR data does not exceed 0.5% of the total carbon content in the samples. It turned out that the symmetry of the EPR signal depends on the size of the powder particles, which is possible only if the samples have a considerable conductivity [7]. For a qualitative estimation of the value of the electrical conductivity of the samples of powders with a particle size of ~ 500 μm we used the ratio of the amplitude of that part of the asymmetric line which corresponds to lower and higher values of the field (A/B). To samples with a lower specific resistance, there corresponds a higher value of the ratio A/B. The symmetry of the shape of the lines of coarse particles at 77 K may be ascribed to the decrease in electric conductivity of the samples, which confirms the semi-conductor character of the conductivity of these samples [1].

The positive value of $g\text{-}g_{el}$, where g_{el} is the factor of spectroscopic splitting of free electrons and is 2.0023, indicates the Hall nature of the paramagnetic centres. Starting from the concentration dependence of the intensity of EPR signal (Fig. 2a) and possible models of paramagnetic centres, there are indications that the paramagnetic absorption at carbon concentrations of 0 to 13% is due to centres which are formed by introducing one carbon atom into the lattice of α-boron in

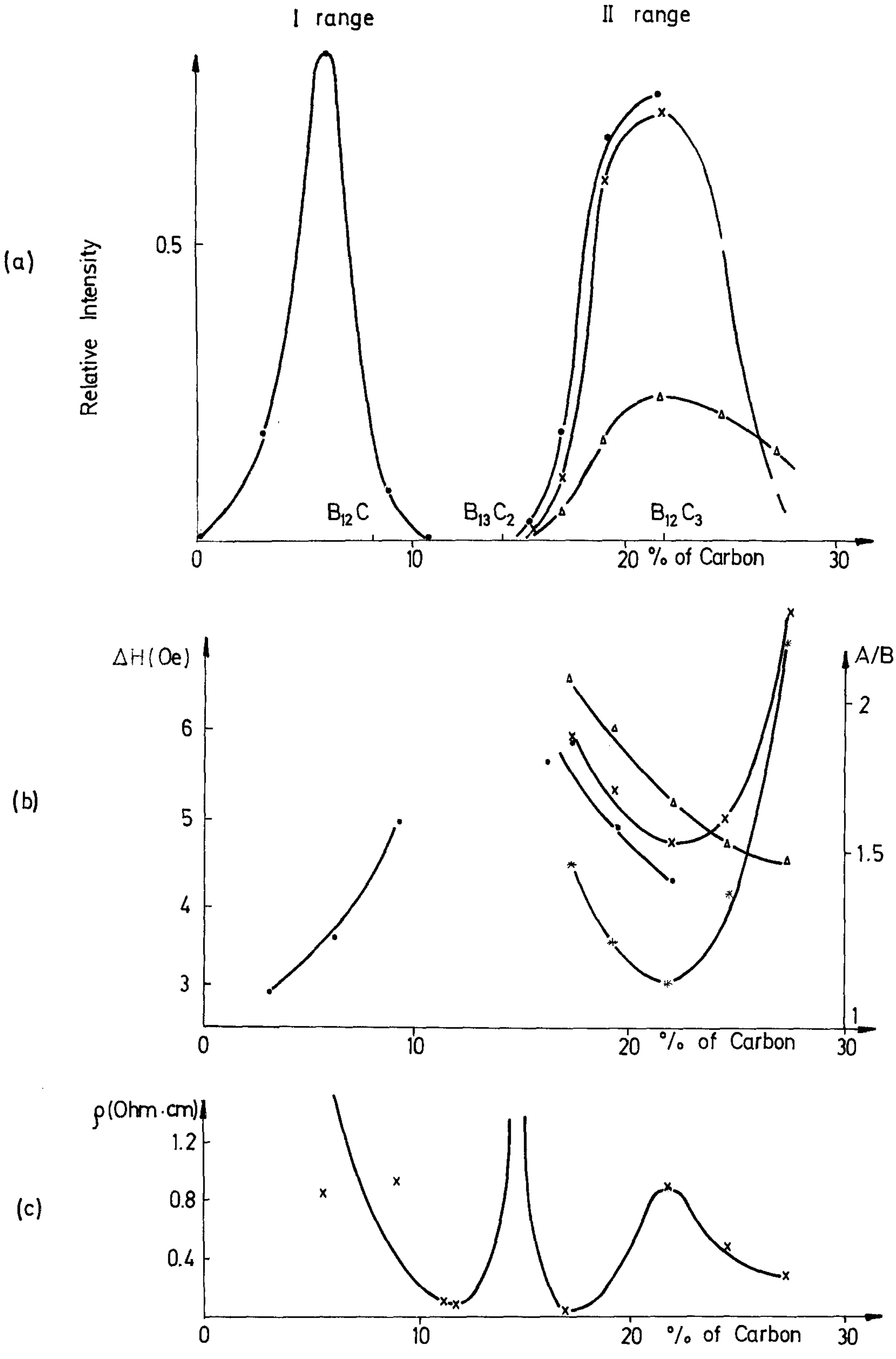

Figure 2 The concentration dependence of the intensity (a), width (b) EPR spectrum, and electrical resistivity (c) [8] of the samples in the B–C system. △ – no. 1; x – no. 2; ● – no. 3; * – the ratio A/B for the samples 2.

the site 2c ($B_{12}C$). The formation of the $B_{12}C$ complex was considered by Zhuravlev *et al.* [8]. In addition to the lattice of $B_{12}C$, in this concentration range (range I) centres of the type $B_{12}C_2$, $B_{12}C_3$ and $B_{13}C_2$ may also exist. The quantitative ratio of individual centres is determined by the conditions of sample preparation.

Let us analyse briefly the specificity of these centres. $B_{12}C_3$ should not have any paramagnetic properties because of the compensation of carbon bonds. As regards $B_{12}C_2$, possible variants of the arrangement of two carbon atoms on the diagonal of the rhombohedron assume the formation of paramagnetic centres, although the properties of these centres should differ from the behaviour of the registered signal. The absence of EPR spectra in the carbon concentration range most suitable for the formation of centres of the $B_{13}C_2$ type indicates either small relaxation times of these centres or unsuitable conditions of formation.

The production and increase in intensity of the EPR signal with further increase in carbon concentration, with a maximum value at ~ 22% (range II, Fig. 2a), may be associated with the $B_{12}C_4$ centres. A model of such a paramagnetic centre predicts the introduction of a fourth diagonal carbon atom into the site 2c′ of the lattice of $B_{12}C_3$. Three sp^3-orbitals of such an atom should form bonds with three boron atoms (site $6h_2$), while the fourth, uncompensated bond gives rise to the observed signal. Such an introduction should shift three remaining carbon atoms along the diagonal and cause a change in the electrical conductivity of the samples. It is known, for example, that β-rhombohedral boron has a high specific electrical resistivity [1]. This is due to the complex character of interatomic bonds, whereby a relatively easy exchange of electrons inside icosahedra is ensured, with a practically complete absence of electron exchange between neighbouring icosahedra. Carbon atoms, entering the boron lattice, facilitate electron exchange between neighbouring icosahedra, bringing about a decrease in electrical resistivity of the samples. The introduction of a fourth carbon atom into $B_{12}C_3$ shifts the chain of three carbon atoms (2c-1b-2c) and prolongs the bonds between boron atoms which are in site $6h_1$ and carbon atom in site 2c, bringing about a change in electrical resistivity. It should be stressed that the increase from 0.06 to 0.9 Ω cm (Fig. 2b) in range II cannot be associated with the formation of ~ 1% $B_{12}C_4$ lattice, so that, evidently, the basic change in electrical resistivity of the samples is due to the complete construction of the $B_{12}C_3$ lattice.

Starting from the total intensity of the EPR signal, the concentration of the solid carbon solution in $B_{12}C_3$ is limited to about 0.5%. From a comparison of the intensity of the signals of synthetized and sintered samples, it is seen that there is a quantitative dependence of the formation of the solid solution on the conditions of preparation. In samples 1, with a carbon concentration higher than 22%, obtained at the same temperature, the number of paramagnetic centres is almost proportional to the number of $B_{12}C_3$ phases, i.e. the concentration of the solid carbon solution in $B_{12}C_3$ is constant for the case given. A more sudden decrease in the intensity of the lines in samples 2 in the same concentration range is probably due to temperature limitations in the formation of the solid solution.

The absence of correlation between the results obtained in the investigation of the electrical resistivity of the samples and the intensity of the EPR spectra (Fig. 2a, c), may be ascribed to a weakening of the effect of paramagnetic centres on the general character of electrical conductivity. It should be stressed that in range II the change in the asymmetry parameter A/B of EPR lines is analogous to the change in electrical resistance (Fig. 2b, c).

The regularity of the change of line width in the investigated concentration range of the components (Fig. 2b) cannot be explained by dipole–dipole and exchange interaction between paramagnetic centres. A comparison of the results obtained in the investigation of the electrical conductivity [8] and the widths of EPR lines indicates an essential interrelationship between these quantities. It is evident that the change ΔH is due to the exchange interaction between unconjugated bonds, which give the EPR signal, and the charge carriers, which may be described by the following spin-Hamiltonian [9]:

$$\mathscr{H} = JsS_{\mathrm{ch}}$$

where J is the exchange integral, s is the spin of the unconjugated bond, equal to $\frac{1}{2}$, S_{ch} is the spin density of charge carriers in the position of unconjugated bond. The rate of relaxation of localized spins, like the rate of nuclear relaxation in metals, is proportional to J. Since the concen-

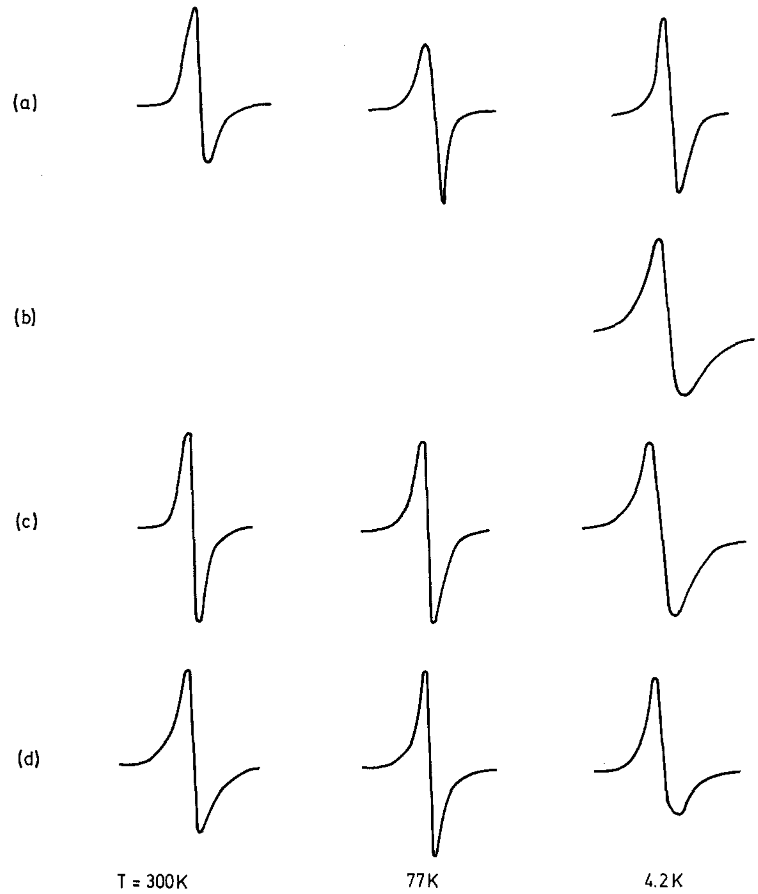

Figure 3 The shape of the EPR spectrum in the 8 mm range at 300, 77 and 4.2 K. (a) Samples 3, 7.2% C. (b) Samples 3, 16% C. (c) Samples 3, 22% C. (d) B–C–5% Ti samples.

tration change of electrical conductivity may be related to the change in the value of the exchange integral J at a constant spin density S_{ch}, the broadening of the EPR line should be analogous to the change in electrical conductivity σ.

The absence of significant differences between signal parameters in two concentration ranges also stimulated measurements in the 8 mm range (Table II and Fig. 3), which confirmed the assumption of the essential difference in the nature of signals in ranges I and II. The asymmetry of signals, their Gaussian form in range I, indicate basically a complex mechanism of formation of lines, associated first of all with the anisotropy of the **g**-factor and the hyperfine interaction of unconjugated carbon bonds with the nuclear spins of neighbouring boron atoms. The symmetrical line of the Lorentzian form in range II speaks in favour of one mechanism of broadening due to a change in relaxation time.

Thus in both cases, paramagnetic centres may be considered as inorganic radicals, CB_3, whose properties depend to a considerable degree on atomic arrangement. It is quite possible that by alloying other modifications of boron by carbon, radicals of the same type are formed, which would naturally have somewhat different properties.

In samples 3 with 16% carbon, an intense asymmetrical signal was observed only at 4.2 K (Fig. 3 and Table II). It most probably may be ascribed to electrons, whose degree of localization is determined by the measurement temperature.

3.2. EPR in the B–C–Ti and B–C–Cr systems

Starting from the conditions of sample preparation, one should expect the formation of paramagnetic centres characteristic of the concentration range II of the B–C system. The change in signal intensity in the 3 cm range at a temperature of 300 K, on an increase in concentration of additions (Table I), indicates different mechanisms of interaction of the basic components in this system. One of these mechanisms predicts the introduction of metal atoms into the lattice and hence a rearrangement of boron and carbon concentrations in the B–C system. The other predicts an incomplete reaction in the solid phase and hence a variation in boron

TABLE II The basic characteristics of the EPR spectrum in the B–C and B–C–Me systems at frequency ~ 35,880 MHz

Samples	Temp. (K)	g factor	$\Delta H_{\max}$	The shape of the line
3 7.2% C	300	2.0028 ± 0.0003	5.3	Asymmetrical, $A/B \approx 1.9$. The influence of the free electrons is not excluded
	77	2.0038 ± 0.0003	6.2	Asymmetrical, $A/B \approx 0.66$.
	4.2	2.0038 ± 0.0003	12.6	Asymmetrical, $A/B \approx 1.2$. Almost Gaussian.
3	300		No signal	
16% C	77		No signal	
	4.2	2.0032 ± 0.0003	20	Asymmetrical, $A/B \approx 1.5$. The shape of the line Lorentzian with $\Delta H = 10$ Oe, $g_\perp = 2.0039$ and $g_\parallel = 2.004$
3	300	2.0029	4.5	Symmetrical almost Lorentzian
22% C	77	2.0033	9.1	Symmetrical almost Lorentzian
	4.2	2.0035	18.0	Lorentzian
B–C–5% Ti	300	2.0025	5.2	Lorentzian
	77	2.0030	3.4	Lorentzian
	4.2	2.0035	12.0	Asymmetrical, $A/B \approx 2.2$. The shape of the individual line Lorentzian with $\Delta H = 5$ Oe, $g_\perp = 2.0037$ and $g_\parallel = 2.0014$
B–C–7% Cr	4.2	2.0034	15.9	Asymmetrical, $A/B \approx 1.4$.

and carbon concentrations, characteristic of range II. However, temperature measurements in the 8 mm range revealed differences in the EPR signals in the B–C–5% Ti, B–C–7% Cr samples and samples 3 with 22% carbon. Keeping in mind that the microhardness of samples increases and the intensity of the EPR signal decreases with increasing concentration of the additive ion, it is probable that the formation is thus stimulated of a larger quantity of $B_{13}C_2$ lattice which is characterized by a higher microhardness [1].

Thus the proposed scheme of formation of a number of complexes in the B–C system makes it possible to explain qualitatively different physical properties of the samples obtained. Since the process of additional filling of vacancies on the diagonal of the rhombohedron by carbon atoms is of the activation character, for a quantitative description and regulation of the process of synthesis for obtaining materials with prior-determined properties, it is necessary to determine the values of activation energy for the entry of each atom into the basic crystal lattice. This problem may be solved only by simultaneous use of different physical methods.

4. Conclusions

The lack of EPR data on the change in properties in the B–C system over a wide concentration range of components and unique concepts on the nature of paramagnetic centres arising in the lattice rearrangement, stimulated our investigations of the B–C, B–C–Ti and B–C–Cr systems in the range 0 to 30 at % carbon. The investigation was made from the point of view of the formation of interstitial solid solutions of carbon in the boron lattice.

In the B–C system, as the carbon content changed from 0 to 30%, two concentration ranges were registered in which a change occurs in the character of EPR signal: the first from 0 to 13% carbon, and the other where the carbon content was 18 to 30%. An analysis of spectrum parameters (g factor, width, shape and line intensity) indicates that in the first range, the EPR signal is due to $B_{12}C$ complexes, which represent the lattice of α-boron with one carbon atom. In the second range, probably four carbon atoms are introduced, so that we are dealing with the production of $B_{12}C_4$ centres. The concentration dependence of line width may be qualitatively explained by the exchange interaction of uncompensated bonds and charge carriers. Paramagnetic centres may, in both cases, be considered as inorganic radicals, CB_3, whose properties depend to a considerable degree on atomic arrangement. It is quite possible that by alloying other boron forms by carbon, radicals could be formed of the same type that would have somewhat different properties.

The change in signal intensity on introduction and increase of the titanium and chromium contents indicates different mechanisms of interaction of the basic components in this system. Bearing in mind that the microhardness of samples increases and the intensity of the EPR signal decreases as the concentration of additives increases, it is probable that larger quantities of the $B_{13}C_2$-phase are thus formed, which is characterized by a higher microhardness.

The proposed scheme of formation of a number of complexes in the B–C system makes it possible to qualitatively explain different physical properties of the obtained materials, although for an integral solution of this problem a wider approach is needed which would unify various physical studies.

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