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Abstract

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X-RAY EMISSION K_α BAND OF CARBON IN TITANIUM CARBIDES, DIAMOND, AND GRAPHITE

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A systematic x-ray spectral study of carbides of transition metals and other interstitial phases was begun with an investigation of the state of transition-metal atoms in these compounds ($^{1-3}$). The first of them, as the most typical representative of this group of substances, was titanium carbide TiC, which has a wide region of phase homogeneity with a NaCl-type f.c.c. lattice (^{1,5}).

X-ray spectra provide valuable information on the number, shape, position, and degree of overlap of the energy bands of the metal and the nonmetal in the valence band of a compound; they are important for elucidating the nature of the chemical bond and the physicochemical properties of the substance conditioned by it; such information can hardly be obtained by any other methods.

The study of the x-ray spectra of the light metalloids of the beginning of the periodic system was for a comparatively long time hindered by the lack of appropriate apparatus and special research techniques.

The present work supplements the investigations mentioned above with data relating to the x-ray emission spectra of carbon emission in the same TiC specimens in the region of its homogeneity (12-24 wt.% C), which had previously been studied from the K spectra of emission and absorption of titanium in carbides. The method of preparing the alloys and data on their chemical composition have already been reported (^{1,4}). The study was carried out on an ultrasoft x-ray vacuum spectrometer RSM-500 designed by A. P. Lukirskii (^{6}), equipped with a concave diffraction grating of 6-meter radius of curvature, ruled with 600 parallel lines per 1 mm of surface. In order to increase the stability of reflection, the grating was coated with a thin (~ 400 Å) layer of gold. The grazing angle for the carbon K_α line and for the oxygen K_α line in MgO, taken as a reference, was in the range 4-5°. The lines were recorded with a receiving-slit width of 5 μ. Powdered specimens of carbides, graphite (aquadag), and diamond were rubbed with the pestle of an agate mortar into the roughened surface of one and the same anode and were x-rayed by successive rotation of the anode with the targets without breaking the vacuum in the x-ray tube, under completely identical

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operating conditions (current 50 mA, excitation potential 3 kV), characterized by high stability. In order to isolate the targets and the working surface of the grating from vacuum-oil vapors and to improve the vacuum in general (to $5 \cdot 10^{-6}$ mm Hg), three traps with liquid nitrogen were used. Very thorough cleaning of the anode spot of the target from oil vapors and adsorbed gases was also carried out by preliminary half-hour bombardment with a powerful cathode beam.

For recording the radiation, a flow proportional counter was used, with a window in the form of two layers of extremely thin cellulose acetate film obtained by spreading this substance over the surface of water ([6]). Methylal vapor, continuously supplied to the counter from a special device, served as the gas medium for the counter. The pressure drop–

on both sides of the film reached 40–50 mm Hg. The voltage on the counter was 1000 V. The radiation-recording scheme was standard, based on an SSD stand and an EPP-09 self-recording device. Under these conditions a resolving power of the order of 0.01 Å was achieved.

The carbon K_α-bands (CK_α), averaged over three independent records, in homogeneous titanium carbides with 12, 14, 16, 19, 22, and 24 wt.% C, in graphite, and in diamond are presented in Fig. 1. According to theory, this band appears as a result of transitions of carbon $2s, p$-electrons to vacancies in its $1s$-shell, formed in the process of excitation of the x-ray spectrum. The CK_α-band in graphite and diamond was studied in ([7], [8]); according to these works it is located at λ44.4 Å (diamond) and 44.8 Å (graphite), which corresponds to 278.3 and 276.0 eV, respectively. Thus, in the transition from the graphite-like state to diamond there is a shift of the center of gravity of this band by 2.3 eV toward the short-wavelength side. The discrepancy between our data and those cited lies within the accuracy of determination of photon energy (0.2 eV).

Fig. 1. Carbon K_α-bands

Fig. 2. K-absorption bands of graphite and diamond according to Chalkin. The experimental curve for graphite is resolved into components σ and a; b is the level-density curve according to Coulson and Taylor

Graphite, as is known, has a layered structure and a hexagonal packing of atoms in the layers, due to the sp^2-type hybridization of the electron wave functions. The length of the C—C bonds in the "aromatic" layers is 1.44 Å, and the distance between layers is 3.35 Å. The CK_α-band in graphite is interpreted by Coulson ([8]) as a superposition of many electron levels occupied by π- and σ-electrons, which participate in delocalized, "smeared out" over the plane of the layer, bonds of a quasi-metallic type (π-electrons) and localized, directed bonds of covalent type (σ-electrons). Accordingly, the former are responsible for electrical conductivity, the latter for the high ($\sim 3800^{\circ}$) melting temperature of graphite. The structure of diamond is, as is known, a regular spatially localized tetrahedron, provided by sp^3-hybridization of the wave functions.

In the transition from graphite to diamond, an additional "transverse" σ-bond from p-electrons is established between the planar "aromatic" networks of the graphite layers, which is now described not by planar sp^2, but by spatially saturated hybridization of the sp^3 electrons. Apparent-

mV; this occurs due to the involvement of all the π-electrons of graphite in localized covalent σ-bonds, i.e., π-bonds in diamond must be completely absent (which is also consistent with its dielectric constants) ([9]).

From consideration of the curves in Fig. 1, in which, according to Coulson, the π- and σ-subbands are separated (by dotted lines) for graphite and diamond, it follows that the π-band lies energetically higher than the σ-band. Thus, the levels occupied by electrons participating in π-bonds should represent the short-wavelength part of the CK_α band and possess their own intensity maximum. The long-wavelength part of the band, considerably broader, represents levels populated by electrons participating predominantly in σ-bonds. The theoretical calculated curve obtained by Coulson under the assumption that only the π- and σ-functions of the electrons of three $2p$ states and one $2s$ state participate in the formation of the CK_α band reproduces well the experimentally observed band shape in Chalklin' s work ([7]) and in our work. Thus, the calculated width of the π-subband is 5 eV, and that of the σ-subband is about 15 eV, i.e., three times larger. The experimental width of the CK_α band according to Chalklin is 18 eV for graphite and 13 eV for diamond. We obtained, respectively, 17.2 eV for graphite and 15 eV for diamond.

Consideration of the shape and position of the CK_α band in homogeneous titanium carbides convinces us that, while no clear dependence of either of these parameters on the carbon concentration in the carbide is found, they are in many respects (apart from perhaps only a small difference in width) similar to one another and occupy a certain intermediate position between the bands of graphite and diamond, being closer in shape to diamond than to graphite, and in width considerably inferior to both. The fine structure of the CK_α band of carbon in carbides remains unchanged throughout the entire investigated range of carbon concentrations, in which a single-phase region with a face-centered cubic lattice of metallic atoms exists. Some (up to 15%) broadening of the band is observed with increasing concentration of C as the vacant sites in the carbide lattice are filled, up to $C = 19\%$. The smoothing of the short-wavelength CK_α maximum in diamond in comparison with graphite and its complete absence in homogeneous carbides make it possible, by analogy with diamond, to conclude that the carbon electrons participate only in spatially saturated covalent hybrid bonds, but no longer sp^3 as in diamond, rather d^2sp^3, which ensure the stability of the carbide lattice. π-bonds of carbon origin in the carbide apparently are completely absent, as are direct C—C bonds; and the comparatively high electrical conductivity retained in titanium carbide is probably due to $4s$ electrons of metallic origin, whose degree of delocalization in the carbide must be fairly large. This agrees with the conclusions of quantum-mechanical calculations ($^{10-12}$).

The degree of covalency of the bond in titanium carbide on the side of the carbon electrons is naturally smaller than in diamond, as indicated by the intermediate position of CK_α for TiC (0.5 eV from diamond). Holliday recorded a difference of the same order in the short-wavelength shift of CK_α in the transition from graphite to carbide and diamond for NbC and ZrC in his preliminary communication (^{13}). However, the covalent bond in titanium carbide considerably predominates over the metallic one. This conclusion is also supported by the invariance, found in work (^{1}), of the shape and position of the $K_{\beta 5}$ emission band and the titanium K absorption spectrum within the homogeneity region of TiC. The ionic bond in the carbide is evidently to be regarded only as a certain degree of polarization of the covalent bond.

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