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THEORETICAL INORGANIC CHEMISTRY

Electronic Structure of Boron Nitride Nanotubes Intercalated with Transition Metals

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Abstract—The electronic structure of semiconductor (5,5) boron nitride nanotubes intercalated with 3*d* metals has been studied by quantum-chemical methods. The linear augmented-cylindrical-wave method has been used for calculating the total and partial densities of electronic states as a function of metal concentration and nature and the structure of the carbon shell. Metallized nanowires based on (5,5) BN nanotubes with one, two, three, and four metal atoms in the cross section have been calculated. The introduction of metals is accompanied by the insulator-to-metal transition of the nanotubes. For forty inorganic materials, we have determined the total densities of states of the valence band and the conduction band and the density of states at the Fermi level, which determines the concentration of free electrons that can be involved in ballistic charge transport in the nanotube. The introduction of metals not only has an effect on the conductive state of the boron nitride nanotube but also change the whole pattern of the valence band of the nanotube, in particular, increases the valence band width by 2–10 eV owing to the low-energy shift of the boron and nitrogen states.

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Advances in synthesis of carbon nanotubes, in studying their properties, and in design of molecular electronics elements on them have stimulated the search for non-carbon nanotubes. The first starting material for creation of non-carbon nanotubes, which
1 2 attracted attention, was an isoelectronic and isostructural analogue of graphite, boron nitride. Boron nitride nanotubes have been synthesized by laser ablation of hexagonal BN, arc discharge between HfB_2 electrodes in a nitrogen atmosphere, and chemical vapor deposition [1–19]. However, even before the synthesis of boron nitride nanotubes, their electronic properties were calculated by quantum-chemical methods with parameterization based on the band structure of hexagonal BN [20]. The calculations predicted that, unlike the carbon nanotubes that can have semiconducting, semimetallic, or metallic properties, depending on the structure, all boron nitride nanotubes should be wide-gap insulators. This is caused by the polarity of the B–N chemical bond and, hence, by the effect of antisymmetric component of the electron potential on the band structure of a compound. More definite electronic properties of boron nitride nanotubes can be technologically advantageous from the viewpoint of their possible applications in nanoelectronics: this fact can facilitate the preparation of nanowires with more reproducible characteristics.

The structure of such BN nanotubes can be visualized as a band cut out of a hexagonal boron nitride layer and rolled up into a cylinder. The geometry of a nanotube is determined by the structure of the cutout band and is characterized by a pair of integers (n, m). The nanotubes have an inner cavity, which can be filled with, for example, metals (M), as shown in Fig. 1. The structure of the resulting compounds is designated as M_n@BN. The present study focuses on the electronic structure of similar nanotubes doped with 3*d* metals from Sc to Zn. Interest in such modified nanotubes is caused, in particular, by that the design of molecular electronic devices and their integration into circuits requires nanowires with different electrical and optical properties, and chemical modification of nanotubes is one of the possible methods of change of these properties. The properties of doped BN nanotubes have been theoretically and experimentally addressed in numerous publications [21–30]; however, except [21, 28], they have dealt with studying the effect of doped main-group elements.

Since the electronic band structure of boron nitride nanotubes is insensitive to variation of their geometry (diameter and chirality), in studying the effect of intercalation on the properties of BN nanotubes, calculations can be restricted to one tube. In this study, calculations are performed for a nonchiral (5, 5) BN nanotube; the effect of transition metals on a (5, 5) carbon nanotube has been studied previously [31].

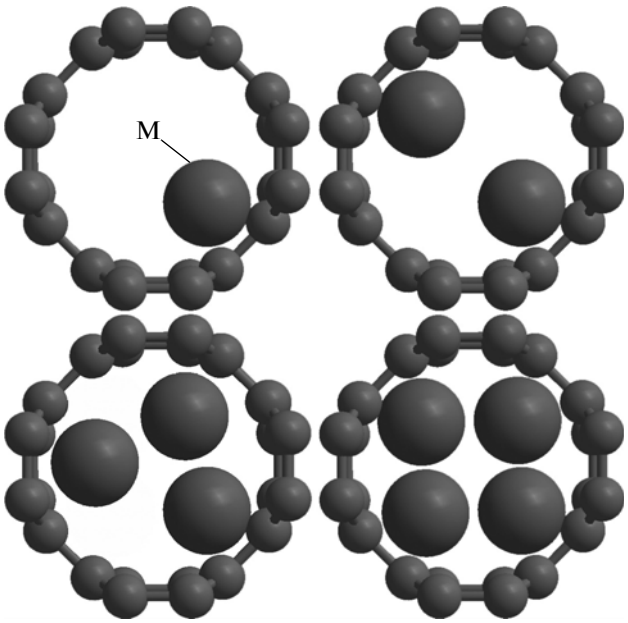

Fig. 1. Cross-section of intercalated boron nitride nanotubes M_n@BN (n = 1–4).

COMPUTATIONAL DETAILS

For calculation of the electronic band structure of nanotubes, we have developed the linear augmented-cylindrical-wave (LACW) method [32]. We consider a one-electron model, and the problem of calculation of electronic levels is reduced to the solution of the one-electron Schrödinger equation. For constructing the electron potential, the local density functional approximation for exchange interaction is used. Each atom of the system is surrounded by a sphere where the potential is taken to be spherically symmetric, and in the interspherical space, the potential is assumed to be 3
constant. In nanotubes with the inner hollow channel filled with metal atoms, the electron motion is confined to a cylindrical region, which is considered by introducing an external electron impenetrable cylindrical barrier. Here, the radius of the latter is taken to be the same as in pure undoped nanotubes. The elec- 4
tronic spectrum of the system is determined by the free electron motion in the interatomic space, electron scattering on atom centers, and reflection of electrons from the barrier [4–6]. Judging by the atomic radii of elements, the cross-section of the inner channel of the (5,5) BN nanotube can accommodate up to four metal atoms.

COMPUTATION RESULTS

Figures 2–6 show the total densities of states of electrons in the pristine armchair (5,5) boron nitride nanotubes and in such nanotubes intercalated with one, two, three, and four metal atoms. As is seen in Fig. 2, the pristine (5,5) nanotube is an insulator; the Fermi level is located in the middle of the gap between the valence and conduction bands. The introduction

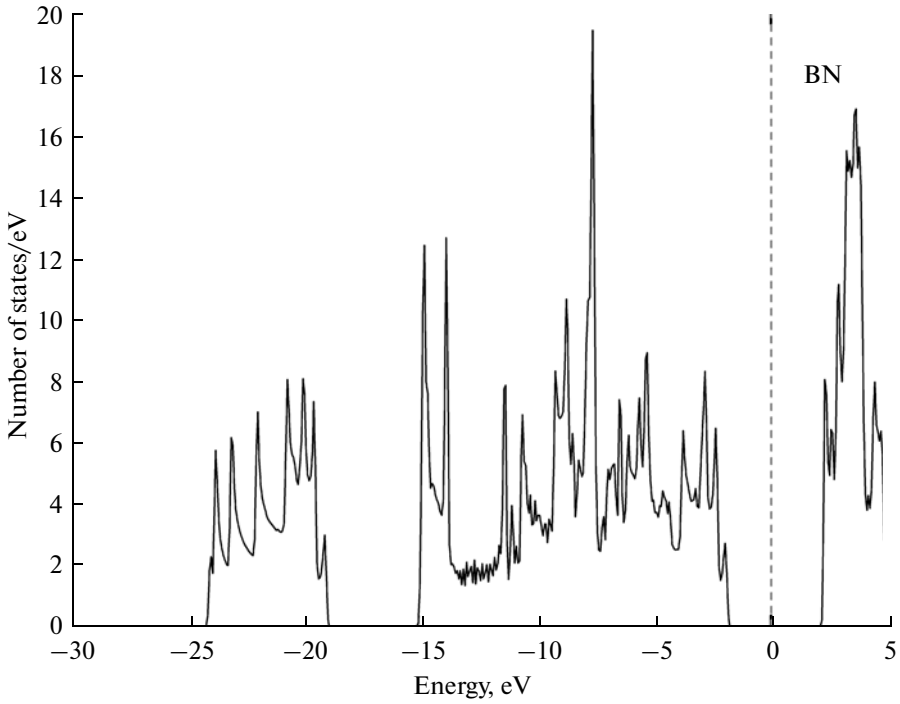

Fig. 2. Total densities of states in a (5, 5) nanotube. Hereinafter, the energies are referenced to the Fermi level.

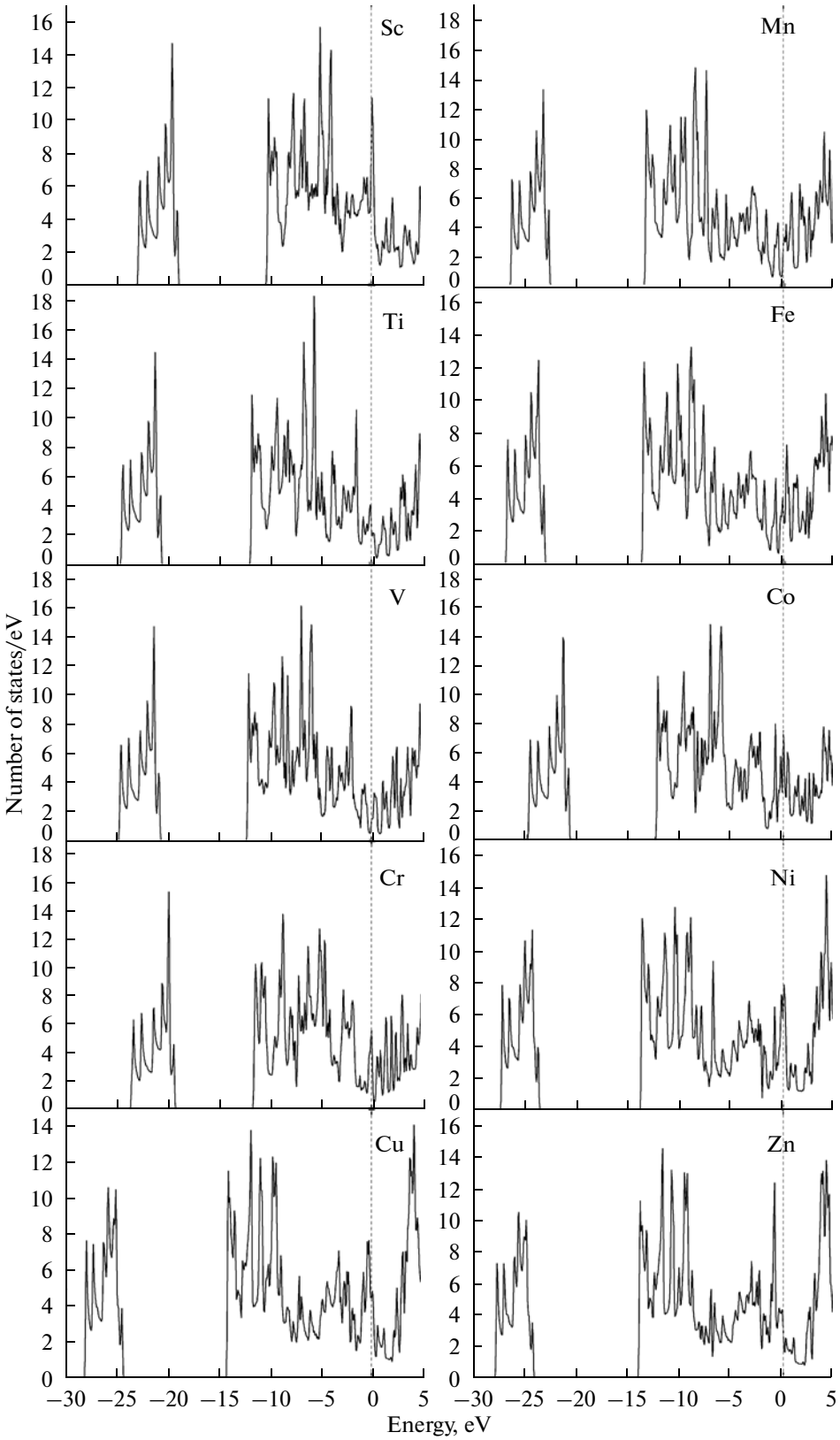

Fig. 3. Total densities of states in a (5, 5) M_1@BN nanotube.

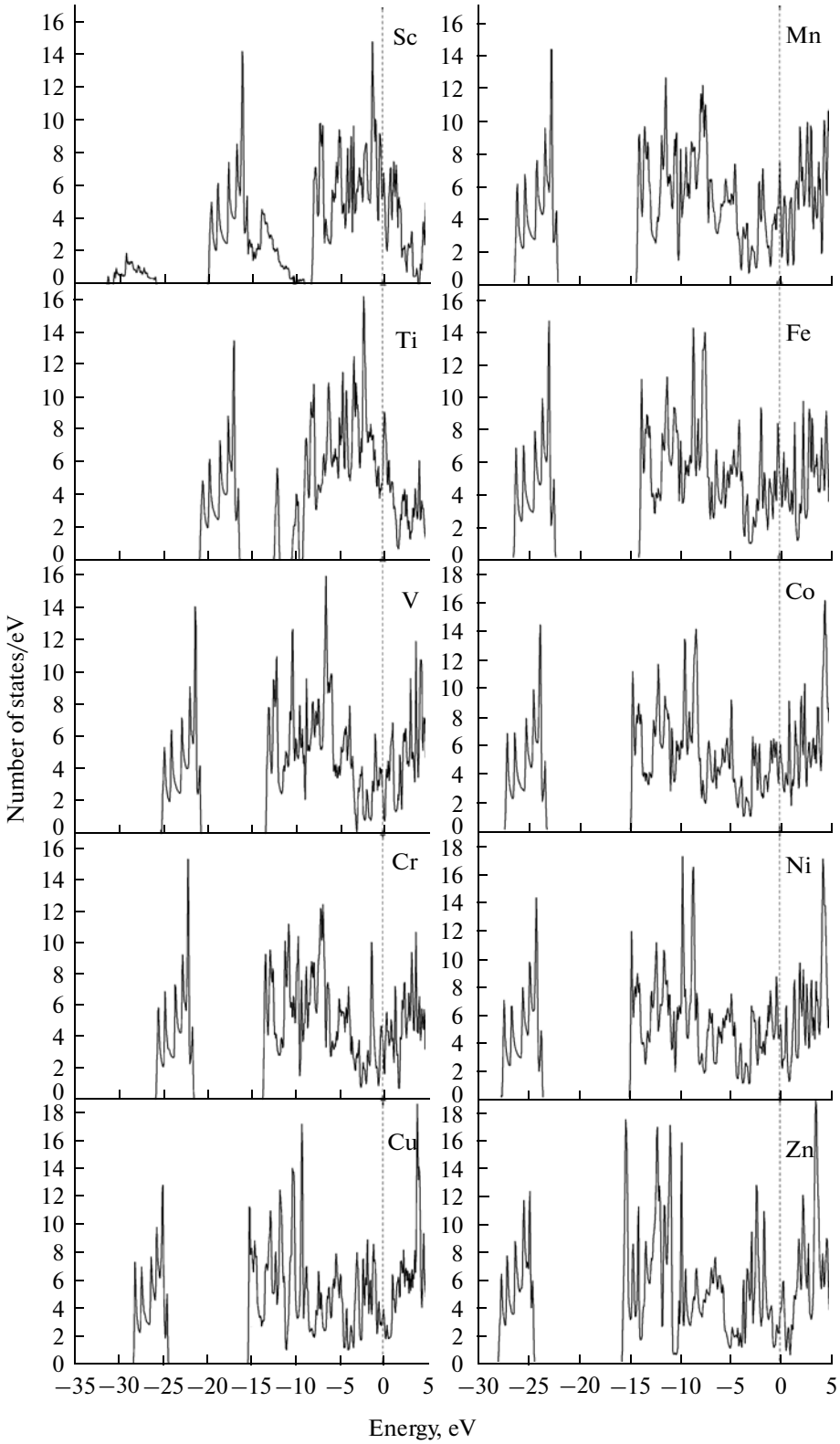

Fig. 4. Total densities of states in a (5, 5) M_2@BN nanotube.

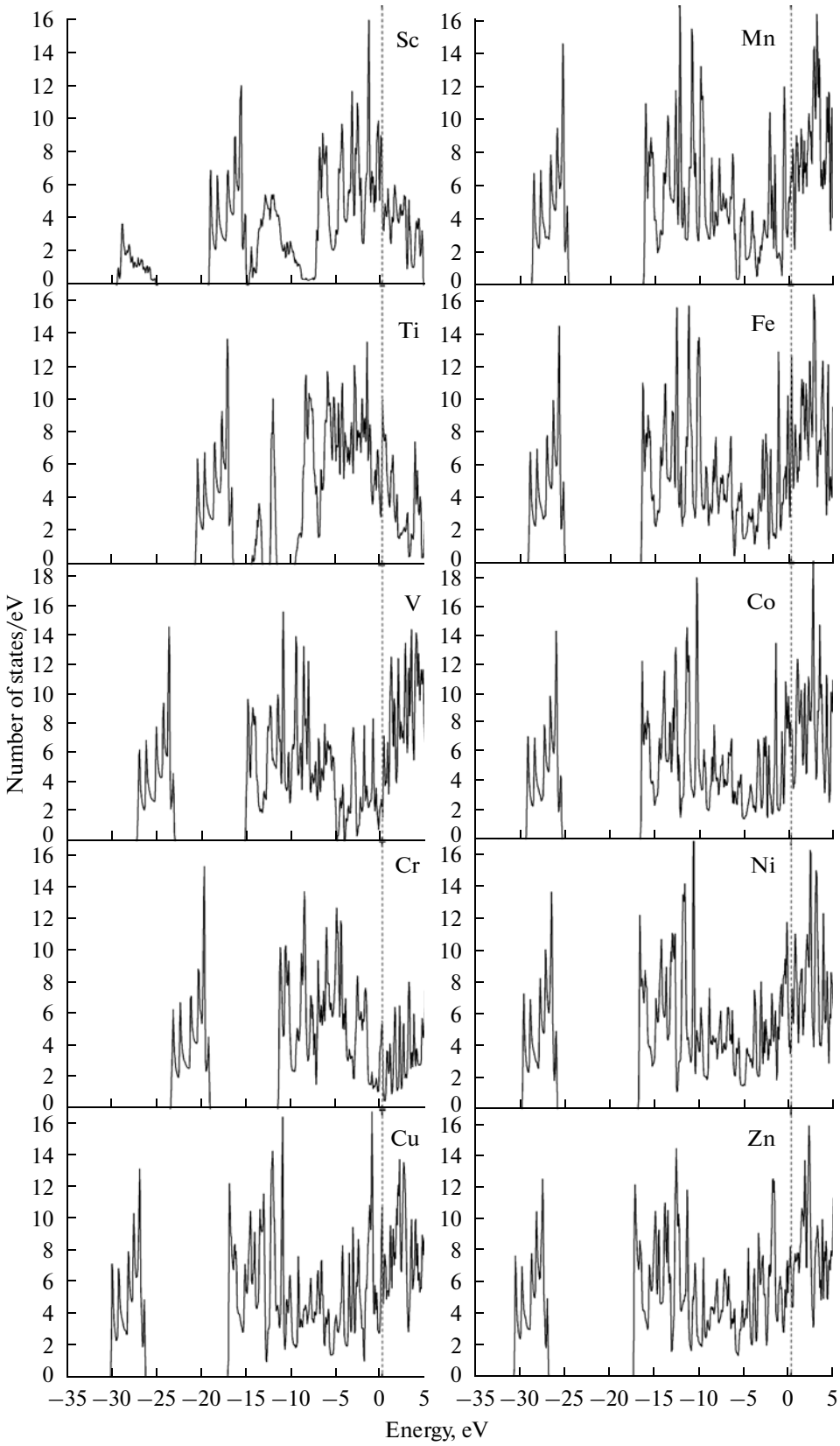

Fig. 5. Total densities of states in a (5, 5) M_3@BN nanotube.

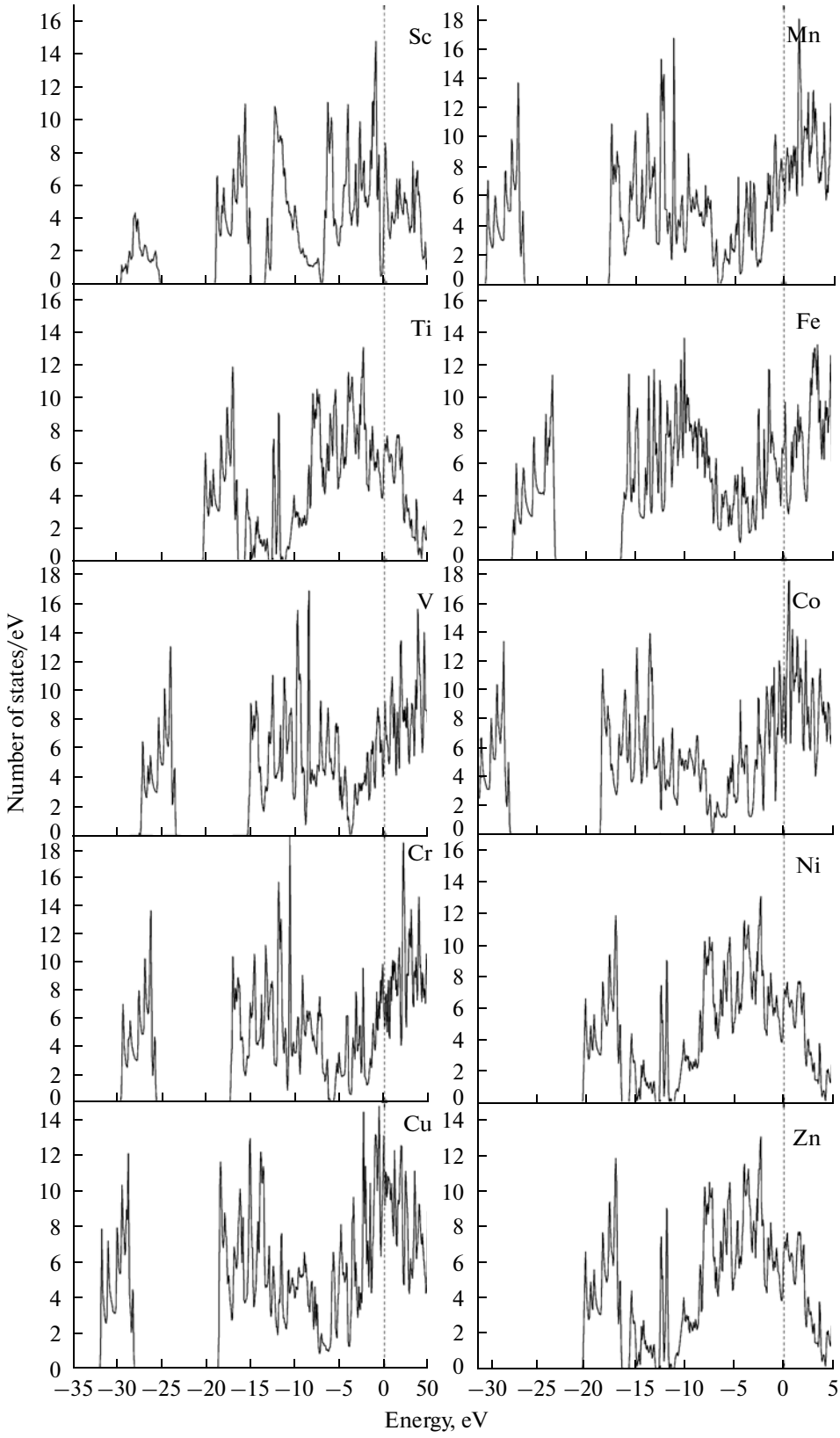

Fig. 6. Total densities of states in a (5, 5) M_4@BN nanotube.

Table 1. Density of states at the Fermi level (states/eV/unit cell) in M_n@BN (5,5) nanotubes (n = 1–4)

M	Number of atoms			
	1	2	3	4
Sc	9.126	5.256	6.896	5.969
Ti	2.428	4.68	6.659	6.823
V	1.525	2.633	2.226	7.737
Cr	5.649	3.867	5.649	5.251
Mn	2.93	7.48	6.885	7.215
Fe	3.099	5.164	10.635	7.09
Co	7.5	5.813	7.82	11.029
Ni	6.75	4.578	3.849	6.823
Cu	4.502	3.661	10.99	11.026
Zn	2.692	3.59	6.224	6.823

Table 2. Valence band width (eV) for M_n@BN (5,5) compounds

M	Number of atoms			
	1	2	3	4
Sc	22.7	31.7	29.1	29.2
Ti	24.6	21.2	21.4	21.1
V	24.9	25.0	26.8	27.4
Cr	23.7	26.1	23.4	29.7
Mn	27.1	26.5	28.1	30.2
Fe	27.5	26.7	28.4	27.5
Co	25.0	27.4	28.9	32.2
Ni	27.6	27.5	29.9	20.6
Cu	28.0	28.1	30.2	32.1
Zn	28.0	27.7	31.3	20.6

of any number of transition metal atoms dramatically changes the pattern: the gap at the Fermi level is filled, and the electron concentration at the Fermi level increases, being as large as 1.525–11.029 states/eV per unit cell (Table 1). The densities of states of nanotubes with one transition metal atom are within the range 1.525–9.126 states/eV, the maximum being observed for the nanowire with a scandium core. As expected, the density of states at the Fermi level increases with increasing metal concentration, but its maximum value is observed in compounds with three Fe atoms and four Co and Cu atoms where the Fermi level exactly coincides with the peak of the density of states curve. As the content of a transition metal and its atomic number increase, the valence band width of the compounds increases from 22.5 eV in Sc@(5,5) to 32.1 eV in Cu_4@(5, 5) and Zn_4(10,0) (Table 2). Such a strong change in the valence band width can be used for analysis of the composition and structure of intercalated compounds, for example, by X-ray spectroscopy.

Thus, the introduction of 3*d* metals is accompanied by a sharp change in the electronic structure boron nitride nanotubes. The pristine boron nitride nanotubes are insulators with a band gap width up to 5 eV, whereas all intercalated BN tubes have a metal-like band structure.

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SPELL: 1. isoelectronic, 2. isostructural, 3. interspherical, 4. undoped