General and Inorganic Chemistry

Crystal and electronic structure of $Ni_3Bi_2S_2$ (parkerite)

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The crystal structure of parkerite, $Ni_3Bi_2S_2$, was studied by single-crystal X-ray diffraction analysis and refined. The single crystal was prepared by the method of chemical transport reactions. The electronic structure of $Ni_3Bi_2S_2$ was calculated by the extended Hückel and DFT—LMTO—ASA methods. Substantial delocalization of electrons in the vicinity of the Fermi level and the presence of the strong Ni—S and Ni—Bi bonds were revealed. The Ni—Ni bonds are weak, which is in agreement with the X-ray diffraction data.

Key words: nickel, bismuth, sulfides, heterometallic bonds, crystal structure, electronic structure, quantum-chemical calculations.

Lower mixed chalcogenides of transition and main-group metals belong to a poorly studied class of inorganic compounds, which are of interest from the standpoint of the possibility for the formation of infinite systems of heterometallic bonds in their crystal structures and the resulting manifestation of unusual electrophysical and magnetic properties. Among these compounds are, in particular, mixed sulfides and selenides of bismuth and Group VIII metals with the structure of the mineral parkerite $Ni_3Bi_2S_2$.[1]

Presently, mixed Bi—Pd and Bi—Rh sulfides[2] of analogous composition and Bi—Ni [3] and Bi—Pd [2] selenides along with parkerite are assigned to this family. All the above-mentioned phases, except for $Ni_3Bi_2Se_2$ for which the corresponding data are lacking in the literature, are typical metals.[4] The $Ni_3Bi_2S_2$ compound exhibits the Pauli paramagnetic properties.[5] Previously, only two phases of this group, *viz.*, $Ni_3Bi_2S_2$ [1] and $Ni_3Bi_2Se_2$,[3] have been studied by X-ray diffraction analysis.

The structure of synthetic parkerite $Ni_3Bi_2S_2$ was established[1] based on the X-ray diffraction data collected from a single crystal, which was grown from a melt quenched starting with 600 °C. The compound crystallizes in the orthorhombic system with the unit cell parameters a = 5.545(4) Å, b = 5.731(3) Å, c = 4.052(3) Å, the space group *Pmam*, Z = 1. However, the high value R_1 = 9.6%, the refinement of the structure with isotropic thermal parameters for the nickel atoms, and the very short Ni—S distances found[1] (2.02 and 2.05 Å compared to the average distance of ~2.3 Å in nickel sulfides[6,7]) cast some doubt upon the reliability of the structure solution.

More recently, specimens, which have been prepared by chemical transport reactions ($AlCl_3$ as the carrier)[9]

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and additionally annealed after grinding[8], have been thoroughly studied by the X-ray powder diffraction method. Based on the results of these studies, the authors suggested that the monoclinic unit cell with the parameters a = 11.074 Å, b = 8.091 Å, c = 7.970 Å, β = 134.0° (the space group $C2/m$, Z = 4) must be chosen for the structure of parkerite. It was concluded[8] that the nickel atoms are located in three completely occupied independent positions rather than in two positions one of which is statistically occupied with the occupancy of 1/2, as has been mentioned previously.[1]

In the present study, we refined the crystal structure of $Ni_3Bi_2S_2$ and analyzed its electronic structure based on the results of quantum-chemical calculations performed for the first time.

Experimental

A specimen of $Ni_3Bi_2S_2$ was synthesized by annealing of a stoichiometric mixture of Ni (99.9% purity), S (high-purity grade), and Bi (99.999% purity) in an evacuated sealed quartz tube at 600 °C for 7 days. The annealed specimen was obtained as a gray sinter with a metallic luster. The X-ray diffraction pattern (a STADI/P (STOE) diffractometer, Cu-$K_{\alpha 1}$ radiation) of the specimen was in complete agreement with the data for $Ni_3Bi_2S_2$.[8]

To prepare single crystals, a mixture of a weighed sample of the resulting phase (~1 mmol) and elemental iodine (high-purity grade, ~0.01 mmol) was sealed in an evacuated quartz tube (15 cm in length and 8 mm in diameter), which was placed in a horizontal furnace with a temperature gradient. The charge was kept at 670 °C and the "cold" end of the tube was kept at 615 °C. After 3 days, dark-gray crystals (of linear dimensions of ~0.1 mm) with a metallic luster were obtained in the "cold" zone of the tube. The crystals were well-faceted but without a pronounced habitus. The X-ray diffraction data were collected on a CAD-4F (Nonius) diffractometer at ~20 °C.

Results and Discussion

The details of X-ray diffraction study and the characteristics of the refinement of the crystal structure are given in Table 1.

Indexing of 15 reflections found in the course of the initial search was performed using the parameters given in Table 1. The X-ray diffraction data set collected in the present study cannot be reindexed with the use of the transformation matrix

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1/2 & 0 & 1/2 \end{vmatrix}$$

in the unit cell published previously[8,9] because in this case the indices of one-half of reflections become noninteger. Hence, it can be concluded that the structure solution within the larger unit cell is correct and this structure is, apparently, a superstructure with respect to that described previously.[8,9] Analysis of the equivalent reflections demonstrated that, in spite of the metric orthogonality of the unit cell parameters, the crystal structure belongs to the monoclinic system with β = 90°. The unit cell parameters were refined based on 24 reflections collected in the angle range of 15.28° < θ < 17.34°. The systematic absence conditions ($h + k = 2n$ for all reflections) indicated the C-centered unit cell and three possible space groups, *viz.*, $C2$, Cm, and $C2/m$. The structure was solved within the most symmetrical space group $C2/m$. The positions of the Bi atoms were located from the Patterson function using the SHELXS-97 program package.[10] The positions of the S and Ni atoms were revealed from a series of subsequent difference Fourier syntheses alternated with cycles of the least-squares refinement. The final refinement (SHELXL-97)[10] of the crystal structure based on F^2 with anisotropic thermal parameters for all atoms converged to R_1 = 0.0570. The positional and thermal parameters are given in Table 2. The crystal structure of the compound is shown in Fig. 1.

Table 1. Details of X-ray diffraction study and refinement of the crystal structure

Parameter	Value
Formula	$Ni_3Bi_2S_2$
Space group	$C2/m$ (№ 12)
a/Å	11.065(2)
b/Å	8.078(2)
c/Å	11.451(2)
β/deg	89.98(2)
V/Å^3	1023.53
Z	8
d_{exp}/g cm^{-3}	8.543
μ/mm^{-1}	80.02
Radiation	Mo-Kα
λ/Å	0.71069
Angle range/deg	3.12 < θ < 27.97
Total number of reflections	5159
Number of independent reflections	1302 (R_{int} = 0.0856)
Number of parameters in the refienement	78
R_1, wR_2 ($F_0 > 4\sigma(F_0)$)	0.0570, 0.1235
R_1, wR_2 based on all reflections	0.1077, 0.1437
Maximum heights of difference peaks, e/Å^3	4.422, −3.714
Figure of merit based on F^2	1.003
Extinction coefficient	0.00026(3)

The crystal structure of $Ni_3Bi_2S_2$ can be represented as a three-dimensional framework formed by the heterometallic Bi—Ni (d(Ni—Bi) ≈ 2.70—2.96 Å) and Ni—S (d(Ni—S) ≈ 2.18—2.19 Å) bonds. The Ni—Bi distances in nickel—bismuth intermetallides (~2.7 Å)[11,12] are close to the values observed in the structure under consideration. The Ni—S distances in crystalline nickel sulfides, for example, in NiS and Ni_3S_2, are generally[6,7] in the range of 2.25—2.4 Å. However, d(Ni—S) = 2.184 Å was found[13] in Ni_9S_8, which is in agreement with the Ni—S distances found in the present study. At the same time, the Ni—Ni distances in the structure of $Ni_3Bi_2S_2$ under study are substantially larger (>2.75 Å) than the corresponding value in metallic nickel

Table 2. Positional and thermal parameters for $Ni_3Bi_2S_2$

Atom	Position	*x/a*	*y/b*	*z/c*	$U_{eq} \cdot 10^4$ /Å^2
Bi(1)	4i	0.1246(1)	0	0.3766(1)	13(1)
Bi(2)	4i	0.3756(1)	0	0.1234(1)	13(1)
Bi(3)	4i	0.6228(1)	0	0.3853(1)	25(1)
Bi(4)	4i	0.8764(1)	0	0.1182(1)	7(1)
Ni(1)	4e	1/4	−1/4	0	17(1)
Ni(2)	4f	1/4	1/4	1/2	17(1)
Ni(3)	8j	1/2	−0.2624(5)	1/2	16(1)
Ni(4)	4g	1	−0.2635(5)	0	16(1)
Ni(5)	4i	0.3757(4)	0	0.3588(4)	17(1)
Ni(6)	4i	0.1246(4)	0	0.1403(4)	17(1)
S(1)	8j	0.3748(6)	−0.2709(7)	0.3531(6)	16(1)
S(2)	8j	0.1260(6)	−0.2708(7)	0.1468(6)	14(1)

(2.49 Å).[14] The shortest Bi—Bi, Bi—S, and S—S distances in the structure of parkerite are 3.78, 3.27, and 3.66 Å, respectively, and are, apparently, nonbonded.

Six independent Ni atoms each are surrounded by four Bi atoms and two S atoms, which form a distorted octahedron with the S atoms in the *trans* positions with respect to one another. The nearest environment about each Bi atom is formed by six Ni atoms. The Bi atoms are additionally surrounded by eight S atoms at distances of >3.75 Å to form a distorted cube. In the structure, two modes of coordination about the bismuth atoms are observed (Fig. 2). Each S atom is bound to three Ni atoms, which do not lie in a single plane with S.

As mentioned previously,[2] the crystal structure of parkerite can be represented as a distorted structure of the CsCl type formed by Bi and S atoms. In this case, Ni atoms are located in the centers of the faces of the distorted cube (octahedral cavities), one-half of faces along the [100], [010], and [001] directions of the cube being occupied. It should be noted that free channels of dimensions of ~4 Å are present in the crystal structure along the [110] direction.

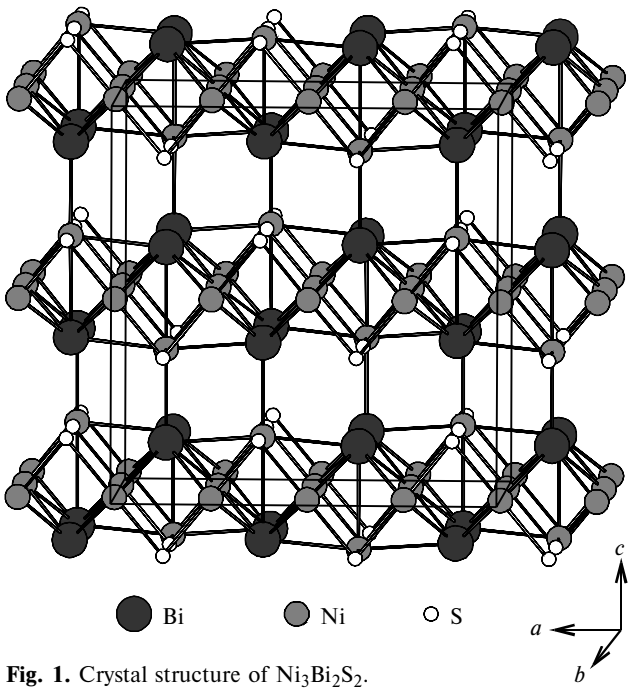

Fig. 1. Crystal structure of $Ni_3Bi_2S_2$.

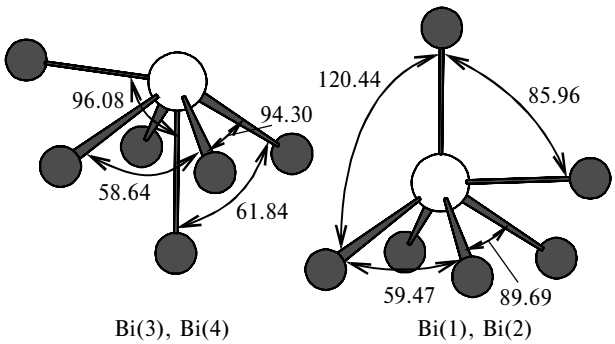

Fig. 2. Nearest environment about the Bi atoms (the bond angles are given in degrees).

Therefore, $Ni_3Bi_2S_2$ and $Ni_3Bi_2Se_2$ cannot be considered as complete structural analogs although the modes of arrangement of the atoms in these structures are very similar. The selenium-containing parkerite crystallizes[3] in the monoclinic system with the unit cell parameters close to those proposed previously[8,9] for $Ni_3Bi_2S_2$.

Quantum-chemical calculations

The electronic structure of the crystal was calculated by the extended Hückel method (EHM) with the use of the YaEHMOP program package[15] and by the density functional theory (DFT) using the LMTO (linear muffin-tin orbitals)—ASA (atomic sphere approximation) method[16] with the use of the LMTO ELECTRONS-II program package.[17] Calculations by the extended Hückel method made it possible to analyze the crystal orbital overlap populations (COOP) for individual chemical bonds of interest. Such analysis cannot be performed within the framework of this method with the use of the LMTO basis set. To simplify calculations, the crystal structure of $Ni_3Bi_2S_2$ was reduced to a sublattice analogous to that of $Ni_3Bi_2Se_2$ by decreasing the unit-cell volume by half. In this case, the atoms were averaged as follows: Bi(1) and Bi(2) merged into Bi1, Bi(3) and Bi(4) merged into Bi2, Ni(1) and Ni(2) merged into Ni3, Ni(3) and Ni(4) merged into Ni1, Ni(5) and Ni(6) merged into Ni2, and both S atoms merged into one averaged atom. Then the number of atoms per unit cell was halved by going to the primitive unit cell.

Extended Hückel method. Calculations were carried out at 78 **k** points in the irreducible part of the Brillouin zone with the use of the parameters incorporated in the YaEHMOP program package. The diagrams of the total density of states (DOS) and crystal orbital overlap populations (COOP) for the structure of $Ni_3Bi_2S_2$ are shown in Fig. 3.

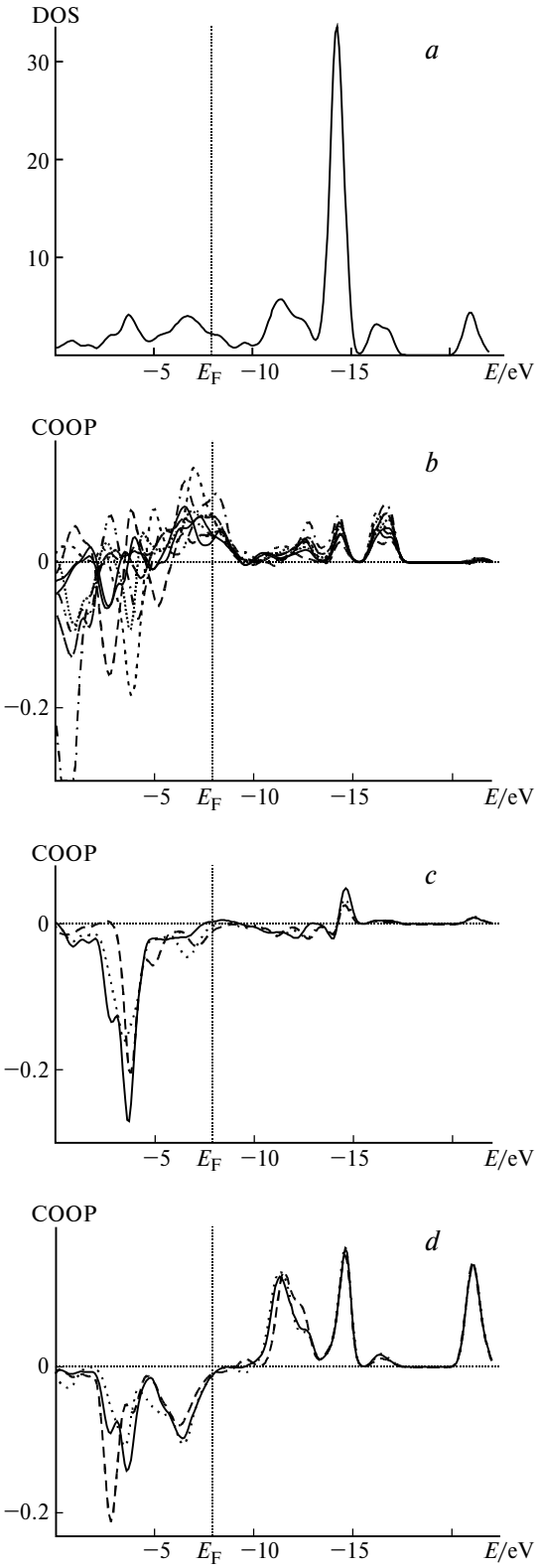

Fig. 3. Density of states (DOS) (*a*) and curves of crystal orbital overlap populations (COOP) for Ni—Bi (*b*), Ni—Ni (*c*), and Ni—S (*d*) in $Ni_3Bi_2S_2$ (EHM). Different lines in the COOP curves correspond to all possible crystallographically nonequivalent bonds of this type. The Fermi level (E_F) is indicated.

According to the results of calculations, $Ni_3Bi_2S_2$ should possess metallic conductivity, which was confirmed by the experimental data.[4] From the COOP curves it follows that the structure is based on a framework formed by the strong Ni—S and Ni—Bi bonds. This conclusion is in complete agreement with our structural data. The Ni—Ni bonds make no noticeable contribution to stabilization of the structure. However, weak interactions between the Ni atoms do occur, as indicated by a small peak in the COOP curve for Ni—Ni at $E \approx -15$ eV.

According to the results of calculations by the extended Hückel method, all d states of the Ni atoms (the high peak at $E \approx -15$ eV, see Fig. 3) are filled, which is indicative of the absence of localized magnetic moments on the Ni atoms. Hence, the compound should exhibit the Pauli paramagnetic properties, which formally agrees with the results of measurements.[5]

DFT—LMTO—ASA method. To obtain an adequate description of the electronic structure of the crystal, six empty atomic spheres per primitive unit cell were additionally introduced (in the positions 8j in the space group $C2/m$) in the centers of faces (which are not occupied by Ni atoms) of the distorted cubic lattice of the CsCl type built of Bi and S atoms. The radii of these spheres were at most 2.64 Å and the charges accumulated in these spheres were 0.32 e per sphere. The local approximation of the electron density with the Vosko—Wilk—Nusair parameters[18] was used. The self-consistent procedure was continued until the change in the electron density became $<10^{-5}$. The valence states included the functions 4sp and 3d for Ni, 6sp and 5d for Bi, 3sp for S, and 1s for empty atomic spheres and were considered taking into account the relativistic corrections. A superposition of the atomic electron densities and the nonmagnetized unit cell was used as the initial approximation. The calculations were carried out in the network consisting of 68 **k** points in the Brillouin zone. To analyze the contributions of the orbitals to chemical bonding, local coordinate systems were used. In the case of the Ni atoms, the *XYZ* axes were directed along the bonds between the nickel atoms and the ligands (the $0Y$ axis was located along the S—Ni—S line). In the case of the S atoms, the *XYZ* axes were directed along the bonds with the Ni atoms.

The calculated diagrams of densities of states are shown in Figs. 4—6. The densities of the s and p states for the single independent S atom in the local coordinate system and for two independent Bi atoms are shown in Figs. 4 and 5, respectively. For the Ni2 atom, the densities of the s, p, and d states in the local coordinate system are shown in Fig. 6. Further analysis was performed for the Ni2 atom. The environments about the remaining two Ni atoms differ only slightly from that about Ni2 and, consequently, the differences in the density of states are insignificant, which was confirmed by calculations.

It can be seen from the above-considered data that $Ni_3Bi_2S_2$ should exhibit metallic properties, which is

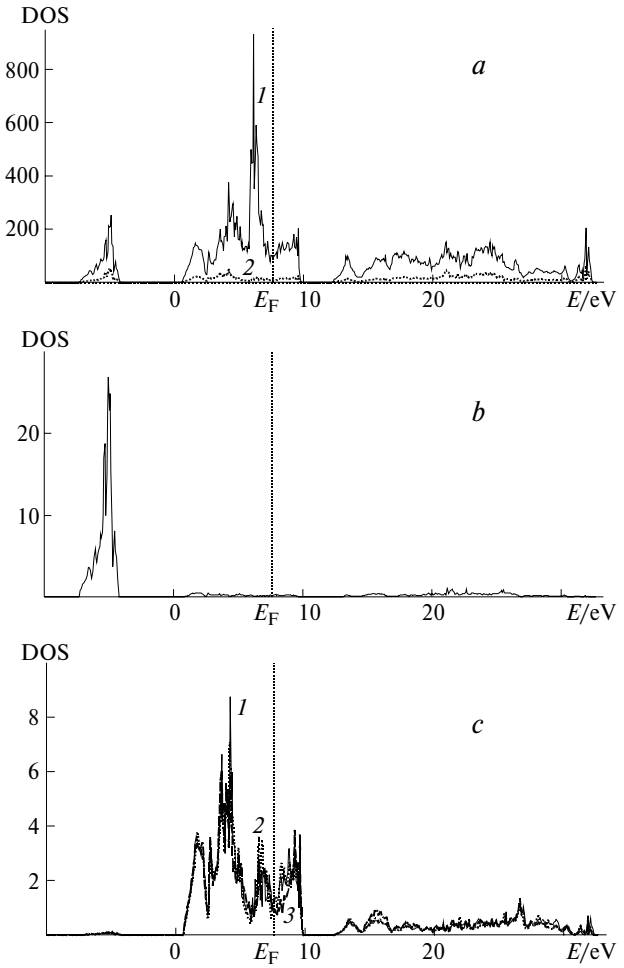

Fig. 4. Overall density of states (*a*, curve *1*), the density of states of the S atoms (*a*, curve *2*), and the densities of states of the 3s (*b*) and 3p orbitals of the S atoms (*c*; curves *1*, *2*, and *3* correspond to the $3p_x$, $3p_y$, and $3p_z$ orbitals, respectively) in $Ni_3Bi_2S_2$ (DFT—LMTO—ASA). The densities of states of the S atoms are given in the local coordinate system. The Fermi level (E_F) is indicated.

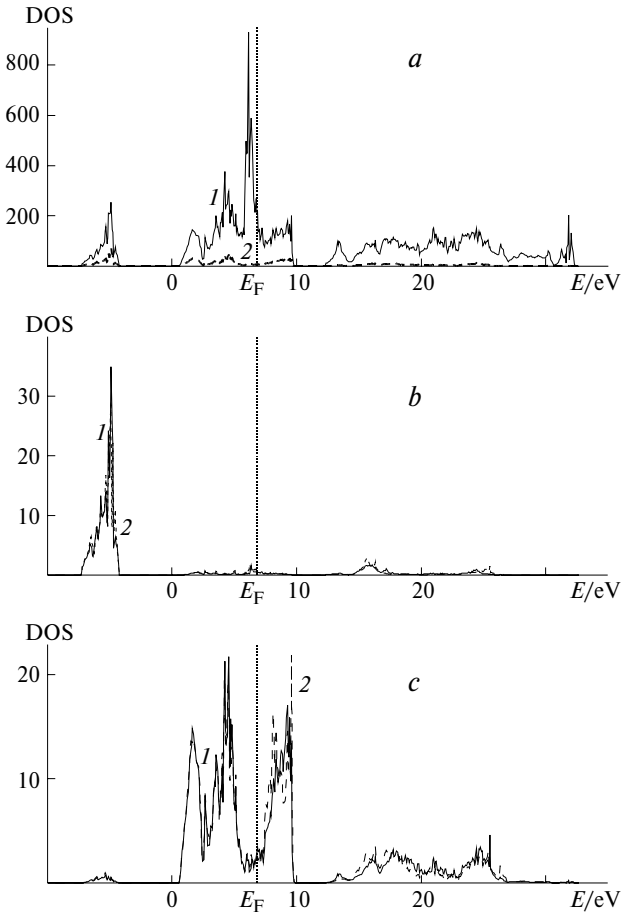

Fig. 5. Overall density of states (*a*, curve *1*), the overall curve of the density of states of the Bi1 and Bi2 atoms (*a*, curve *2*), and the densities of states of the 6s (*b*) and 6p (*c*) orbitals of the Bi1 (*1*) and Bi2 (*2*) atoms in $Ni_3Bi_2S_2$ (DFT—LMTO—ASA). The Fermi level (E_F) is indicated.

also evident from the results of calculations by the extended Hückel method. The states in the vicinity of the Fermi level (see Figs. 4 and 5) are formed by the p states of the bismuth and sulfur atoms and the d states of the nickel atoms. Since all states in the vicinity of the Fermi level in this compound are substantially delocalized, it is difficult to assign particular charges to the atoms. It can be asserted that the s states of the p elements, three d states (*xz*, *yz*, *xy*) of the Ni atoms, and the lower-lying atomic levels of these elements are filled. It is conceivable that the lone s electron pair of the Bi atom is stereochemically active and leads to asymmetry of its coordination environment. Other states are substantially mixed and the remaining 26 electrons (four 3p electrons at each S atom, three 6p electrons at each Bi atom, and four 3d electrons at each Ni atom) belong to these states. The Pauli paramagnetism of this compound as well as its metallic properties may result from the fact that the d states of the nickel atoms, which are only partially occupied, are substantially delocalized.

The differences between the densities of the p_x, p_y, and p_z states of the S atom in the local coordinate system are insignificant, and these orbitals are responsible for the formation of three σ bonds with the Ni atoms. Due to asymmetry of the coordination environment about the bismuth atom, its p states are substantially mixed and it is difficult to carry out more detailed analysis of interactions between bismuth and nickel. The Ni atoms have a slightly distorted octahedral environment such that three orbitals corresponding to π interactions (*xz, yz, xy*) with the adjacent atoms are split to a lesser extent (peaks are less diffuse, see Fig. 6) than the z^2 and $x^2 - y^2$ orbitals (see Fig. 6), which are intersected by the Fermi level. The $x^2 - y^2$, *xy*, and *yz* orbitals corresponding to dπ—pπ interactions with the S atoms are split more substantially than the z^2 and *xy* orbitals, which interact only with the bismuth atoms. Hence, it can be concluded that the interactions of the Ni atoms with the Bi atoms are weaker than those with the S

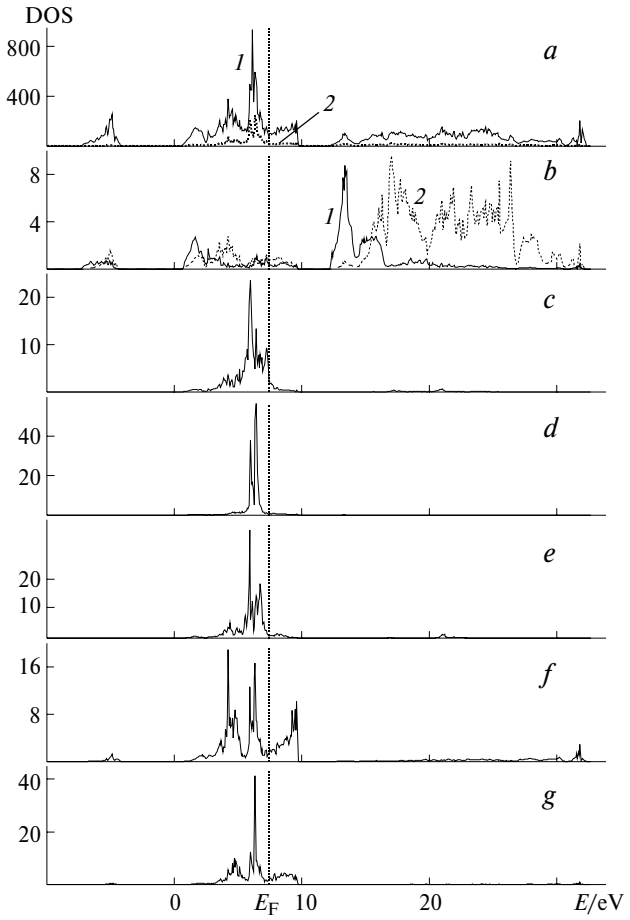

Fig. 6. Overall density of states (*a*, curve *1*), the density of states of the Ni2 atoms (*a*, curve *2*), and the densities of states of the 4s (*b*, curve *1*), 4p (*b*, curve *2*), $3yz$ (*c*), $3xz$ (*d*), $3xy$ (*e*), $3x^2 - y^2$ (*f*), and $3z^2$ (*g*) orbitals of the Ni2 atoms in $Ni_3Bi_2S_2$ (DFT—LMTO—ASA). The densities of states of the Ni2 atoms are given in the local coordinate system. The Fermi level (E_F) is indicated.

atoms. As one would expect, this is particularly true of the dπ—pπ interaction (the narrow peak of the *xz* states).

* * *

Therefore, the X-ray diffraction data and the results of quantum-chemical calculations demonstrated that the crystal structure of parkerite is based on a three-dimensional framework formed by the heterometallic Ni—Bi bonds. This framewrok is additionally stabilized by coordination with the S atoms. Interactions between the Ni atoms in the compound under consideration are very weak. According to the results of DFT—LMTO—ASA quantum-chemical calculations, the states in the vicinity of the Fermi level are substantially delocalized over all Ni, Bi, and S atoms.

Mixed lower nickel—bismuth iodides are most similar in chemical properties to compounds with the parkerite structure. The crystal structures of nickel—bismuth subiodides $Bi_{5.6}Ni_5I$ [19] and $Bi_{12}Ni_4I_3$ [20] are based on frameworks of heterometallic Ni—Bi bonds with the minimum distance d(Ni—Bi) ≈ 2.6 Å. The Bi—Bi distances in lower iodides are also long (>3.25 Å). However, the sulfur atoms in $Ni_3Bi_2S_2$ are coordinated to the transition metal atoms, whereas the iodide ions in subiodides are located at distances of ~3.5—3.6 Å from the Bi atoms and, apparently, these distances can be considered as nonbonded. The minimum I—Ni distances are no larger than 3.5 Å. In addition, the shortest distances between the Ni atoms in the structures of subiodides are ~2.6 Å, *i.e.*, the subiodides, unlike parkerite, contain homometallic Ni—Ni bonds. The above-considered structural features of lower nickel—bismuth iodides are in good agreement with the results of calculations of their electronic structures by the extended Hückel method.[19,20]

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