

CHEMICAL BONDS IN SOLIDS

Volume 4: Semiconductor Crystals,
Glasses, and Liquids

CHEMICAL BONDS IN SOLIDS

Volume 1: General Problems and Electron Structure of Crystals

Volume 2: Crystal Structure, Lattice Properties, and Chemical Bonds

Volume 3: X-Ray and Thermodynamic Investigations

Volume 4: Semiconductor Crystals, Glasses, and Liquids

CHEMICAL BONDS IN SOLIDS

*Proceedings of the International Symposium on Chemical Bonds in
Semiconducting Crystals held in Minsk, USSR, in 1967*

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Volume 4: Semiconductor Crystals,
Glasses, and Liquids



CONSULTANTS BUREAU • NEW YORK-LONDON • 1972

This series of four volumes is comprised of articles appearing in *Khimicheskaya Svyaz' v Kristallakh* and *Khimicheskaya Svyaz' v Poluprovodnikakh* (Minsk: Nauka i Tekhnika, 1969). The articles are arranged topically and have been revised and corrected by the editor for this edition. The exact source of each article appears in a footnote on the opening page of that article.

Many of the articles by non-Russian authors are printed from manuscripts kindly furnished by the authors.

The present translation is published under an agreement with Mezhdunarodnaya Kniga, the Soviet book export agency.

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ХИМИЧЕСКАЯ СВЯЗЬ В КРИСТАЛЛАХ
KHIMICHESKAYA SVYAZ' V KRISTALLAKH

ХИМИЧЕСКАЯ СВЯЗЬ В ПОЛУПРОВОДНИКАХ
KHIMICHESKAYA SVYAZ' V POLUPROVODNIKAKH

Library of Congress Catalog Card Number 73-185456

ISBN Four-volume set 0-306-17150-3

ISBN 978-1-4684-8684-1 ISBN 978-1-4684-8682-7 (eBook)

DOI 10.1007/978-1-4684-8682-7

© 1972 Consultants Bureau, New York

A Division of Plenum Publishing Corporation
227 West 17th Street, New York, N.Y. 10011

United Kingdom edition published by Consultants Bureau, London
A Division of Plenum Publishing Company, Ltd.
Davis House (4th Floor), 8 Scrubs Lane, Harlesden, London,
NW10 6SE, England

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PREFACE

The present four volumes, published under the collective title of "Chemical Bonds in Solids," are the translation of the two Russian books "Chemical Bonds in Crystals" and "Chemical Bonds in Semiconductors." These contain the papers presented at the Conference on Chemical Bonds held in Minsk between May 28 and June 3, 1967, together with a few other papers (denoted by an asterisk) which have been specially incorporated. Earlier collections (also published by the Nauka i Tekhnika Press of the Belorussian Academy of Sciences) were entitled "Chemical Bonds in Semiconductors and Solids" (1965) and "Chemical Bonds in Semiconductors and Thermodynamics" (1966) and are available in English editions from Consultants Bureau, New York (published in 1967 and 1968, respectively).

The subject of chemical bonds in crystals, including semiconductors, has recently become highly topical and has attracted the interest of a wide circle of physicists, chemists, and engineers.

Until recently, the most successful description of the properties of solids (including semiconductors) has been provided by the band theory, which still dominates the physics of solids. Nevertheless, it is clear that the most universal approach is that based on the general theory of chemical bonds in crystals, in which details of the electron distributions between atoms and of the wave functions appear quite explicitly.

Although, in principle, the general theory is superior to the band theory, the appropriate techniques for its application are not yet developed sufficiently well and a unified approach to a quantitative description of the structures and the physical properties of crystals is still lacking. The less generally valid band theory can at present give clearer and more convincing explanations of changes in the physical properties of crystals caused by variations in the temperature, pressure, magnetic and electric fields intensities, impurity concentrations, etc. However, many problems encountered in the study of chemical bonds in crystals cannot be considered within the framework of the standard band theory. They include, for example, determination of the elastic, thermal, and thermodynamic properties of solids, as well as the structure and properties of liquid and amorphous semiconductors.

Among the most important requirements in the theory of chemical bonds is the development of a unified method for the description of the chemical interaction between atoms, which would be based on the structure of the atomic electron shells and in which one would utilize the wave functions and the electron density distributions calculated for isolated (free) ions on the basis of the data contained in Mendeleev's periodic table of elements. This unified approach should make it possible to elucidate the interrelationship between the various physical properties and the relationship between the equilibrium and the excited energy states in crystals. In contrast to the study of chemical bonds in a molecule, an analysis of the atomic interaction in crystals must make allowances for the presence of many coordination spheres, the long- and short-range symmetry, the long- and short-range order, and other special features of large crystalline ensembles. As mentioned already, the band theory is intimately related to the chemi-

cal interaction between atoms. An analysis of the published experimental and theoretical data shows that the need is urgent, and all the prerequisites now exist, for the development of the proposed unified theory of chemical bonds, which would include, as one of its essential components, an improved band theory following logically from the general concept of chemical bonds in crystals.

Various approaches are possible to the theoretical solution of the problem of chemical bonding. One can solve the problem by the purely theoretical technique of finding wave functions and using quantum-mechanical methods without recourse to any additional empirical constants. Slater pointed out that this is the most direct way although, obviously, it is not the fastest or the most effective. This purely theoretical approach requires the knowledge of wave functions to a high degree of precision. The existing quantum-mechanical methods are approximate. Solutions of the Schrödinger equation for atomic systems depend on the reduction of the problem to the one-electron approximation or, in the case of the many-electron approach, on approximations of varying degrees of precision. These two approaches yield relatively accurate results only if the problem is tackled scrupulously and a very careful allowance is made for the errors committed. In calculations of the energy relationships and of the lengths of atomic bonds in crystals, the required parameters are small differences between large quantities, and therefore considerable errors may be committed if one does not properly control the approximations made.

The established methods of valence bonds and molecular orbitals (MO), including the method of linear combinations of atomic orbitals (LCAO), which have been so successful in the treatment of molecular systems, need further refinement when applied to crystals. The preference for the method of valence bonds in the case of solids is not accidental because it yields clearer results. In contrast, calculations dealing with the simplest molecules are currently tackled usually by the method of molecular orbitals, including the method of absolute, purely theoretical, quantum-mechanical calculations, which is adopted in those cases when a sufficiently precise form of the Hamiltonian operator can be obtained for the system being considered.

Various semiempirical methods of solving the quantum-mechanical problem of the interaction between atoms in a crystal are also of great interest. In these methods, the atomic distances, energies, and interactions are calculated by invoking the mathematical apparatus of quantum mechanics in conjunction with empirical or semiempirical wave functions (including those found experimentally). In spite of its well-known inaccuracies and inconsistencies, the semiempirical method for the quantum-mechanical solution of the problem of chemical bonding in crystals provides the most accurate results for a given amount of work.

The use of experimentally determined wave functions may provide the most effective technique among the semiempirical methods. One way of developing these methods would be to use the statistical approach to chemical bonding in crystals, based on the statistical theory of atoms developed originally by Thomas, Fermi, and Dirac, and more recently by Gombás. The statistical methods have the advantages of simplicity and clarity but they are the least accurate. However, the statistical theory of atoms has recently been refined so that the accuracy of the results obtained is now higher. By way of example, we can cite the book by Gombás which gives the values of the wave functions (atomic orbitals) for all elements in the periodic system. These functions are calculated according to the statistical model of the atom, and are in good agreement with the results of the more complex and more laborious Hartree-Fock calculations.

In many quantum-mechanical calculations, use is made of the wave functions obtained by the Dirac-Slater and the Hartree-Fock methods for the approximate solution of the Schrödinger equation for free atoms. It would be very interesting to determine whether these functions could be refined specifically for crystals and whether the problem could be solved using relatively simple analytic approximations to the calculated functions. In particular, the approximation by Gaussian functions demands attention.

It would also be interesting to examine the possibility of using directly, in quantum-mechanical solutions of problems in the quantum chemistry of crystals, the tabulated data on the wave functions and atomic scattering factors calculated by the Hartree-Fock and Dirac-Slater methods for ions with different degrees of ionization. When the crystal lattice of an element or a compound is formed, the wave functions undergo a slight change which can be allowed for. Therefore, the solution of problems in the quantum chemistry of crystals through the use of the tabulated wave functions of ions with different degrees of ionization, combined with allowance for the crystal field, has definite advantages and provides a promising approach. In particular, the tabulated data can be used to estimate approximately the ionic radii, the band structure, and the bond energies if an allowance is made for the changes introduced by the crystal field.

It follows that, in all these cases, it is desirable and even essential to have sufficiently accurate experimental data which can be used as the basis of comparison with the theoretical values. Thus, the establishment of the experimental quantum chemistry of crystals was a great step forward in the development of a unified quantum-chemical theory of bonds in crystals.

The Minsk conferences on chemical bonds in semiconductor and other crystals have demonstrated clearly the importance of experimental determinations of the distribution of the electron density in crystals, the distribution of the potential in the crystal lattice, and the application of various methods to the calculation of the effective charges of ions and of accurate values of the atomic spacings and bond energies. It has been found possible to estimate various physical properties of crystals from the experimentally and theoretically determined atomic scattering functions and the electron density distributions in crystals. These problems are considered in several papers in the present collection.

The books we are presenting deal with various aspects of chemical bonding in crystals, particularly in semiconductor crystals. In semiconductors, the nature of the chemical bonds can vary within wide limits and extend over a considerable part of the well-known tetrahedron of the metallic, covalent, ionic, and van der Waals types of chemical bond. This tetrahedron is only approximate but it provides a sufficiently clear basis for the classification of transitions which may occur between different types of bond.

Some workers regard the atomic bonds in semiconductors as a special type which is independent of the other four types. It seems clear, however, that the chemical bonds in semiconductors do not represent an independent type of bonding but form the most general class, which extends from the center of the aforementioned tetrahedron to its vertices.

The electron distributions in the atoms forming a crystal, the dimensions of the ions, the ionization potentials, and the type and the energy of the atomic bonds in the crystal, all depend on the positions in Mendeleev's table of the elements forming the crystal. Consequently, an analysis of the changes in the nature of chemical bonds resulting from changes of the positions of a crystal's components in Mendeleev's table provides a convincing and clear picture of the sequence of changes in the nature and the energy of the interaction between atoms.

A characteristic feature of the present state of the science of chemical bonds in crystals is the tendency to combine theoretical and experimental investigations and to close the usual gap between theoretical analyses and experimental studies.

Recent years have seen a considerable extension of the experimental methods used in quantum chemistry and in investigations of the nature of chemical bonds in crystals. It is worth mentioning methods based on the studies of the elastic and the inelastic scattering (by crystals) of x rays, electrons, neutrons, protons, mesons, α and other particles, as well as the x ray spectroscopic methods. Methods based on the use of positron annihilation are also of considerable interest.

Practically inexhaustible possibilities are latent in the methods based on the external and internal photoelectric effects excited by x rays and light of various wavelengths. It is worth mentioning specially the methods of electron (β) spectroscopy, cold emission, photoelectric emission, and photoelectron spectroscopy, the last being used widely for the purpose of chemical analysis.

Investigations of the scattering of x rays, electrons, mesons, and neutrons, carried out under suitable conditions, can provide highly accurate information on the atomic scattering functions, and on the electron and spin densities in crystals.

Improved x-ray spectroscopic methods can be used to find the effective charges of ions and to determine the spectra of the energy states $N(E)$ of the electrons in crystals. These spectra govern many physical properties. Experimental investigations of the dependences of the $N(E)$ spectra of the components (elements and compounds) of crystals on the positions of the elements concerned in Mendeleev's periodic table can give extensive information on some features of chemical bonding.

The density of states $N(E)$, which governs the nature of atomic bonds, is one of the important criteria that determine the transition to the superconducting state in the theories of Bardeen, Copper, Schrieffer, and Bogolyubov. The density of states $N(E)$ can be found directly from the results of x-ray spectroscopic analyses.

The problem of chemical bonding is inseparable from the magnetic properties of crystals. This follows clearly from the work of Klemm, Dorfman, Goodenough, and others who have found that magnetic measurements can provide quantitative information on the type and energy of atomic bonds.

There is little doubt that direct experimental determination of the heats of atomization, heats of formation of compounds, free energies, and other thermodynamic properties of crystals can provide the basis for theoretical calculations of the bond energies, which are used to establish the nature of bonds.

Other important experimental methods for elucidating the nature of chemical bonds in crystals are the study of the elastic and thermal properties and the determination of phonon spectra. Many of these properties can be regarded as thermodynamic stability criteria and are quantitative measures of the second derivatives of the bond energies with respect to the atomic spacing. Moreover, such investigations yield temperature dependences of the characteristic thermodynamic functions.

The cardinal feature of successful investigations of chemical bonds in crystals is the proper combination of theoretical, experimental, and crystallochemical techniques. The crystallochemical aspect of chemical bonding has been stressed particularly clearly by Pauling, Belov, Geller, Goodenough, and others. This aspect is also reflected in the present collection.

The number of experimental physical methods which can provide quantitative information of direct interest in the quantum chemistry of crystals is increasing continuously. Routine use is made of various optical and spectroscopic methods in the investigations of solids. Gamma resonance (Mössbauer effect), Kikoin-Noskov photoelectric and photomagnetic effects, cyclotron resonance, EPR, NMR, and other methods are used widely. Measurements of mechanical properties, whose importance was stressed by A. F. Ioffe, are being used for quantum-chemical purposes but not sufficiently intensively. Many of these methods have been introduced, reached sufficient precision, and yielded satisfactory interpretations only in the last few years. Clearly, the extension of experimental investigations of the mechanics, nature, special features, and energies of chemical bonds in crystals has become a very urgent task.

The guiding principles in these investigations are those enunciated by P. L. Kapitza, who suggested that substances be investigated in extreme or limiting states such as ultra-high purity,

very low temperatures, strong magnetic and electric fields, and high pressures. To these must be added the principles of physiochemical analysis proposed by N. S. Kurnakov, who suggested that investigations be carried out by varying the composition and the external equilibrium parameters.

Our four volumes reflect this tendency to combine theoretical and experimental methods in studies of chemical bonds in crystals.

These volumes contain theoretical and experimental papers on chemical bonds in crystals, especially those in semiconductors and semimetals.

The first volume deals with the general aspects of chemical bonding in crystals and with the interrelationship between the electron structure of crystals and their physical properties.

Some of the papers comprising the first volume deal with those theoretical and experimental aspects of chemical bonds in crystals which relate to the most general rules governing the dependence of the atomic interactions on the positions of the components in Mendeleev's periodic table. The criteria governing the transitions from the metallic to the semiconducting and the superconducting states are also considered.

Professor Sir Nevill Mott deals with the important topic of developing a satisfactory theory of liquid and amorphous semiconductors. Sir Nevill's paper is of great interest because of the heavy stress he lays on the importance of knowing the nature of chemical bonds in liquid and amorphous semiconductors in order to gain an understanding of the special features of the state and properties of these substances.

The first volume also includes papers on the correlation between the magnetic properties, the structure, and the electron distributions in crystals, and on that between the electron interaction, the distributions of the electron densities and potentials, and the band structure. New experimental results are also reported.

The second and the third volumes deal with the correlation between the nature of chemical bonds and the physical properties of crystals, particularly lattice dynamics, and thermodynamic and thermochemical parameters. The second volume is concerned mainly with crystal structure, physical properties, and lattice dynamics. The first part of the third volume reports extensive data on electron distributions and on the effective charges of ions deduced from x-ray diffraction and spectroscopic investigations. The second part of the third volume is concerned mainly with thermodynamic and thermochemical investigations of semiconductor crystals. This part includes also papers concerned with the thermodynamic stability of crystals.

The fourth volume concentrates mainly on the properties of semiconducting compounds, including transition-metal silicides, amorphous and liquid semiconductors, and particularly the nature of the chemical bonds in these materials.

One of the chapters in the fourth volume is devoted primarily to complex semiconducting compounds. Most of the papers comprising this chapter were contributed by the talented scientist N. A. Goryunova (who died prematurely) and her colleagues. In the first paper of this chapter, consideration is given to the methodological aspects of the search for compounds exhibiting semiconducting properties on the basis of Mendeleev's periodic table.

The four volumes are packed with information. Some of the papers are tentative and suggest possible ways of solving problems. The majority give the results of completed investigations. The whole set provides an idea of the present state of the science of chemical bonds in crystals, fills some gaps in our knowledge of the chemical bonding in condensed phases, and should stimulate further studies of this very interesting subject. It is hoped that the wide range of readers engaged in the physics, chemistry, and technology of solids and semiconductors will find something of interest to them in these volumes.

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SEMICONDUCTING PROPERTIES AND CHEMICAL BONDS

CRYSTAL STRUCTURE OF THE COMPOUND Mn_4Si_7 *

O. G. Karpinskii and B. A. Evseev

Homogeneous alloys of the higher manganese silicide were investigated by single-crystal methods of x-ray structure analysis. Several structures were detected in this region, belonging to a tetragonal system and differing in the value of the superlattice constant along the fourfold axis. The crystal structure was studied and the positions of the atoms and the coordinate parameters were determined. The chemical bonds in Mn_4Si_7 are of mixed metal-covalent nature. There are regions in the structure, oriented relative to the *c* axis, which differ in the nature of the atomic interaction. The crystal features of this structure are consistent with the anisotropy of the physical properties of the higher manganese silicide.

The higher silicide of manganese is one of the few compounds of silicon with transition metals which have semiconducting properties. However, the problem of the chemical composition, crystal structure, and nature of this compound are still open questions despite all the work on this substance [1-5].

We carried out an x-ray structure investigation of manganese silicide single crystals obtained by different methods: by horizontal Bridgman method, by pulling from the melt, and so on. The samples studied had compositions within the homogeneity region of the higher manganese silicide.

The crystals were photographed in RKV-86A and KFOR-4 cameras and on a URS-50IM instrument in $Mo K_{\alpha}$ radiation.

It was found that all the crystals were tetragonal (Laue class D_{4h}) and a superlattice was detected along the fourfold axis. The unit cell of the compound could, in this case, be regarded as being made up of several subcells, placed one upon another. Accurate measurements of the position of the $00l$ -type lines showed that the crystals studied had different values of the superlattice constant. This means that in the homogeneity region of the higher manganese silicide there are several structures with different numbers of subcells. The tetragonal subcell is the same for all the structures. It contains four manganese atoms. The symmetry of the arrangement of manganese atoms in the subcell corresponds to the space group $D_{4h}^{19} - I4_1/amd$ (position 4(a)). The dimensions of the subcell are: $a = 5.52 \text{ \AA}$, $c = 4.37 \text{ \AA}$.

We made a detailed study of the crystal structure of the compound with the unit cell composed of four subcells.

*The articles in this volume were originally published in two Russian books, "Khimicheskaya Svyaz' y Kristallakh," published by Nauka i Tekhnika, Minsk, 1969 (hereafter called "Crystals"), and "Khimicheskaya Svyaz' v Poluprovodnikakh," also published by Nauka i Tekhnika, Minsk, 1969 (hereafter called "Semiconductors"). The source of this article is "Semiconductors," pp. 267-272.

TABLE 1. Coordinates of Manganese and Silicon Atoms

Atom	Position	Coordinates		
		<i>x</i>	<i>y</i>	<i>z</i>
Mn I	2 (a)	0	0	0,25
II	2 (c)	0	0	0
III	4 (h)	0,5	0,5	0,125
IV	4 (i)	0	0,5	0,0625
V	4 (i)	0	0,5	0,3125
Si I	8 (j)	0,3436	0,7721	0,0409
II	8 (j)	0,1933	0,1507	0,1129
III	8 (j)	0,1627	0,6791	0,1815
IV	4 (e)	0,3333	0,3333	0,25

The dimensions of the unit cell of this compound, determined with a diffractometer, are: $a = 5.525 \pm 0.001 \text{ \AA}$, $c = 17.463 \pm 0.003 \text{ \AA}$.

Measurements of the volume of the unit cell, the pycnometric density of the compound, and the approximate chemical composition established that the cell contains 44 atoms, 16 of these being manganese atoms and 28 silicon atoms, i.e., the compound has the formula Mn_4Si_7 ($\text{MnSi}_{1.75}$). The x-ray density calculated from these data ($\rho_{25^\circ\text{C}} = 5.186 \text{ g/cm}^3$), is in good agreement with the experimental value ($\rho_{25^\circ\text{C}} = 5.16 \text{ g/cm}^3$).

Systematic extinctions of $0kl$ reflections with $l \neq 2n$ are characteristic of the diffraction pattern of Mn_4Si_7 . The extinction law and the symmetry of the arrangement of manganese atoms in the subcell enable the compound to be placed with certainty in the $D_{2d}^5 - P4c2$ space group.

The manganese atoms occupy five positions in the unit cell: 2(a), 2(c), 4(h), and two 4(i).

To determine the coordinates of these atoms, the intensities of about 300 structurally independent reflections of the $hk0$ and $0kl$ type were measured and analyzed. The reflection intensity was measured by the ionization method. The measurements were made on a spherical crystal of 0.51-mm diameter. The spherical shape was obtained by rolling [6]. Corrections were made for the absorption and for the Lorentz-polarization factor.

The positions of the silicon atoms in the unit cell were determined by analyzing the atomic vector function $P(xy)$ and by the trial-and-error method.

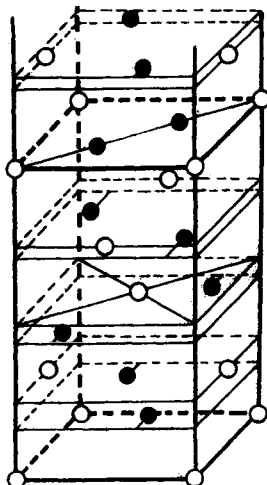


Fig. 1. Subcell of the Mn_4Si_7 structure: O) manganese atoms; ●) silicon atoms.

TABLE 2. Shortest Interatomic Distances in the Structure of Mn_4Si_7

Atom	Neighbor	$r, \text{\AA}$	Number of neighbors	Atom	Neighbor	$r, \text{\AA}$	Number of neighbors
Mn	Mn	2.973	4	Si I	Mn II	2.387	1
					Mn III	2.272	1
Mn I	Si III	2.320	4		Mn IV	2.365	1
	Si IV	2.603	2		Mn IV	2.450	1
					Si II	2.578	1
Mn II	Si I	2.387	4	Si II	Mn II	2.392	1
	Si II	2.392	4		Mn III	2.578	1
					Mn IV	2.375	1
Mn III	Si I	2.272	2		Mn V	2.295	1
	Si II	2.578	2		Si I	2.578	1
	Si III	2.330	2		Si III	2.488	1
	Si IV	2.542	2	Si III	Mn I	2.320	1
Mn IV	Si I	2.365	2		Mn III	2.330	1
	Si I	2.450	2		Mn IV	2.471	1
	Si II	2.375	2		Mn V	2.575	1
	Si III	2.471	2		Mn V	2.650	1
					Si II	2.488	1
Mn V	Si II	2.295	2		Si IV	2.443	1
	Si III	2.575	2	Si IV	Si III	2.674	1
	Si III	2.650	2				
	Si IV	2.330	2		Si IV	2.603	1
					Mn III	2.542	2
					Mn V	2.330	2
					Si III	2.443	2
					Si IV	2.603	1

Silicon atoms occupy four positions in the cell: 4(e) and three 8(j).

The coordinates of the silicon atoms were refined by the method of least squares, using the BÉSM-3M computer and the UMNK program [7]. The final values of the coordinates of manganese and silicon atoms are shown in Table 1. The constant for the temperature factor was $B = -0.252$.

The value of the divergence factor R for 170 nonzero $0kl$ -type reflections was 12.32%; for all 240 reflections, $R = 21.45\%$; for 27 nonzero $hk0$ -type reflections, $R = 13.73\%$; and for all 54 reflections, $R = 18.46\%$.

The subcell of Mn_4Si_7 is depicted in Fig. 1. For clarity, the vertical scale of the figure is magnified by two. As can be seen from the figure, the manganese and silicon atoms in the structure are located in plane layers.

The shortest interatomic distances in the structure of Mn_4Si_7 are shown in Table 2. The distances between the manganese and silicon atoms are accurate to $\pm 0.002 \text{\AA}$, and between the silicon atoms to $\pm 0.003 \text{\AA}$.

An analysis of the interatomic distances shows that the bonds between the atoms in Mn_4Si_7 are of mixed covalent-metallic nature. The distances between manganese atoms in the struc-

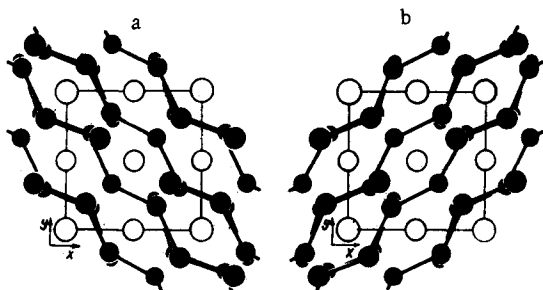


Fig. 2. Projection of the structure of Mn_4Si_7 on the xy plane: a) lower half of cell; b) upper half. The bonds between silicon atoms in the chain are shown by the thick lines.

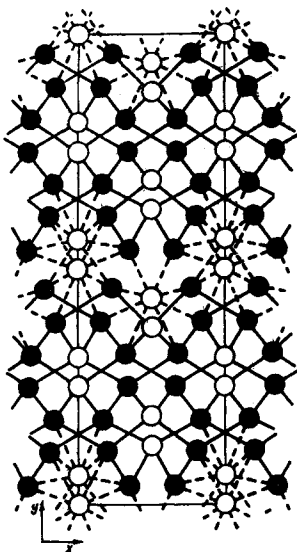


Fig. 3. Projection of the structure of Mn_4Si_7 on the $x0z$ plane.

ture are greater than the sum of the atomic radii; for this reason, the interaction between these atoms can be neglected.

The silicon atoms are linked together in chains. Each chain is made up of seven atoms; the distances between the atoms are: 2.578, 2.488, 2.443, 2.443, 2.488, 2.578 Å. The strongest bond between the silicon atoms is in the middle of the chain; the bonds are weaker towards the ends of the chain, and are then broken. Each chain lies wholly in one half of a unit cell. The orientation of the chains in the upper and lower halves of the cell is different (Fig. 2a,b). The silicon chains are linked by manganese atoms.

The distances between the manganese and silicon atoms in the Mn_4Si_7 structure vary between 2.27 and 2.65 Å. The manganese atoms can be separated into two groups according to their interatomic distance: 1) those for which all the distances between a given atom and adjacent silicon atoms are of the same order (~ 2.4 Å); 2) those for which distances of about 2.3 Å and 2.6 Å both occur. A distance of about 2.6 Å is close to the sum of the metallic radii of manganese and silicon; a distance of 2.3 Å can be considered as close to the sum of the covalent radii of these elements.

A projection of the structure on the $x0z$ plane is shown in Fig. 3. The bonds between manganese atoms of the first group and silicon atoms are shown by the dashed lines. The bonds between silicon atoms and the "covalent" bonds between manganese atoms of the second group and silicon atoms are shown by the continuous lines.

Manganese atoms of different groups in the structure occupy different positions. Manganese atoms of the second group are in the same regions as the silicon chains; those of the first group lie between the ends of the chains. Thus, there are regions in the structure, perpendicular to the c axis, which differ in the nature of the interatomic interaction. This may explain the observed anisotropy of the physical properties of single crystals: the maximum electrical and thermal conductivity are observed in directions perpendicular to the fourfold axis [8].

It has already been shown that there are several structures with different numbers of subcells in the homogeneity region of the higher manganese silicide. The distance between the manganese layers is constant in these structures and it is determined by the size and symmetry of the subcell; the distance between silicon layers is dependent on the chemical composition and is greater than the distance between manganese layers. The difference between the spacings of the manganese and silicon layers leads to the formation of a superlattice with constant c which is an integral multiple of the sublattice constant c' . The compound $Mn_{11}Si_{19}$ has this type of structure [4, 5]; it has a unit cell made up of 11 subcells.

The structure of Mn_4Si_7 is similar to that of $Mn_{11}Si_{19}$ in the nature of the atomic interaction. Our analysis of the structure of $Mn_{11}Si_{19}$ showed that in this structure the manganese atoms are again situated at some distance from each other, and the silicon atoms form chains, the distance between which is greater than the distance between the atoms in the chain. In contrast to Mn_4Si_7 , there are two types of chains, containing four and six silicon atoms, respectively. As in Mn_4Si_7 , the interaction between chains in $Mn_{11}Si_{19}$ is realized through manganese atoms.

The authors would like to express their gratitude to Academician N. V. Ageev for his advice and interest in the work, and also to E. I. Elagina, L. D. Dudkin, and B. K. Voronov for providing the crystals used in the investigation.

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PHYSICOCHEMICAL NATURE OF MONOSILICIDES WITH AN FeSi-TYPE STRUCTURE*

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An analysis of the FeSi-type crystal lattice is used to propose a general scheme of chemical bonds which assumes, essentially, the formation of saturated (two-electron) covalent bonds between metal and silicon atoms and the overlap of wave functions of metal-atom d electrons, forming bands. A study of the electrical properties of cobalt monosilicide single crystals is used as a basis of a two-band energy scheme for free carriers which we assume is due to the partial overlap of two 3d bands of cobalt atoms. The proposed valence scheme, the data on the energy spectrum of free carriers, and the published data on magnetic susceptibility are employed to derive a model for the energy state of valence electrons in cobalt monosilicide. The general structural scheme proposed is extended to other members of this group of compounds (FeSi, MnSi, CrSi); this scheme explains, at least partially, the dependence of the electrical properties of these compounds on the number of 3d electrons in the metal atoms. In particular, the semiconductivity of iron monosilicide below room temperature and the complex nature of the change of thermoelectric power are accounted for.

The FeSi structure type, in which a number of monosilicides and germanides of d-transition metals crystallize [1, 2], is characterized by a cubic unit cell and the $P_{2,3}$ space group. Each atom in the cell is surrounded by seven atoms of the other kind: one very close, three further away, and three at an even greater distance. Each metal atom is associated with six relatively remote similar atoms. The most important crystallographic properties of compounds with a FeSi-type structure are shown in Table 1. Recently, a comparatively large amount of experimental data, which are not always consistent, has been published on the study of the physical properties of 3d-transition metal (Cr, Mn, Fe, Co) monosilicides.

Most of the work on the magnetic susceptibility (χ) of the phases mentioned above was carried out in the 77-800°K temperature range [3-9]. So as not to describe the results of every investigator, we will summarize the data on the magnetic properties of individual compounds.

Chromium monosilicide, formed by a peritectic reaction [10] (this point is essential for a critical evaluation of the results from the point of view of equilibrium of the samples studied), is characterized by an effective magnetic moment (μ_{eff}) which varies in the temperature range investigated and corresponds to a change of the number of unpaired electrons per metal atom from about 1.3 to about 2.5 [4, 6] (these figures are only estimates, since in this case it is possible only to refer nominally to the validity of the Curie-Weiss law in each narrow temperature range).

*"Semiconductors," pp. 273-284 (see page 3).

TABLE 1. Crystallographic Properties of Compounds with a FeSi-Type Structure

Compound	Lattice constant, Å	Parameters of atoms		Interatomic distances, Å				d_{Me}^{\bullet} (coordination no., 7)	$\Delta, \%$
		x_{Me}	x_{Si}	Me—Si (1)	Me—Si (3)	Me—Si (3)	Me—Me (6)		
CrSi	4.608	0.136	0.846	2.32	2.43	2.58	2.83	2.46	13.1
MnSi	4.568	0.138	0.846	2.30	2.39	2.55	2.79	2.52	10.1
FeSi	4.489	0.137	0.842	2.29	2.34	2.52	2.75	2.44	11.2
CoSi	4.438	0.140	0.843	2.28	2.33	2.47	2.73	2.42	11.3
ReSi	4.775	0.14	0.84	—	—	—	2.92	2.66	8.0
CrGe	4.780	—	—	—	—	—	2.93	2.46	16.0

Manganese monosilicide is characterized by a fairly sharply defined value $\mu_{\text{eff}} \approx 2.5 \mu_{\text{B}}$ in the 100–400°K temperature range [3], and by a smooth change of the reciprocal susceptibility at higher temperatures, conventionally corresponding to an increase of μ_{eff} to 4.1 Bohr magnetons [7].

An unusual change of the magnetic susceptibility is observed for iron monosilicide: it increases from approximately zero at liquid-nitrogen temperatures to a maximum value at about 200°C (the temperature of the maximum differs somewhat according to the results of different authors [4, 5, 8]); it then falls and above about 500°C it corresponds to an effective moment of $\sim 2.5 \mu_{\text{B}}$ [8]. From neutron diffraction studies, specially carried out [5], it can be concluded that the extremum of χ_{FeSi} is not due to a change in the crystal structure or to antiferromagnetism.

Cobalt monosilicide has a weak diamagnetism at low temperatures and a small increase of the positive susceptibility above room temperatures [9]. The value and the nature of the change of χ as a function of temperature indicate that there are no unpaired electrons on the Co atoms of CoSi.

Early data on the study of the electrical properties of monosilicides [11–14] were concerned mainly with the electrical conductivity (σ) and the thermoelectric power (α) at room temperature. A number of papers by Russian and foreign authors has been published only in the last 2–3 years on the temperature dependences of α , σ , and the Hall coefficient (R_{H}) of alloys based on CoSi in the 100 to 1000°K temperature range [15, 16] and also on the low-temperature measurements of σ of polycrystalline samples of 3d-transition metal monosilicides [17].

We studied the temperature dependences of the thermoelectric properties of the four compounds mentioned above in the 100 to 1000°K temperature range (low-temperature measurements were carried out on equipment of V. I. Kaidanov). The measurements on Mn, Fe, and Co monosilicides, melting congruently [18], were carried out on single crystals grown by the Czochralski method; equilibrium samples of chromium monosilicide were prepared by vacuum hot pressing of powders made of previously alloyed ingots followed by a homogenizing anneal. Stoichiometric samples were studied and also compositions which deviated from a stoichiometric composition toward either the metal or silicon. No significant differences in the electrical properties were then observed (Table 2). For this reason, the results of measurements at various temperatures are shown in Fig. 1 for stoichiometric compositions only.

Despite the crystallographic isostructure, the electrical properties of monosilicides, as can be seen from the data given, differ markedly both in absolute values and sign and in the nature of the change with temperature. Two of the most important facts are immediately apparent: