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Charge transfer and interface properties in inorganic superstructures and composites

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The processes of charge transfer and electronic reconstruction at interfaces of inorganic superstructures and composites have not yet been adequately investigated. This review integrates and analyzes the results of theoretical and experimental studies of structural and electronic effects at interfaces of metal oxide or chalcogenide superstructures and composites. Charge transfer and, hence, change in interface properties compared to the properties of substructures are shown to be determined by the preparation method of composites and chemical nature of the superstructures, incommensurability of structural parameters and valence states of the constituent metals. The changes are maximal for nanoheterostructures, and the degree of change is related to electronic conductivity of substructures. The macroscopic properties of the composite materials depend on the amount of interfaces in their bulk.
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I. Introduction

Inorganic superstructures and composite materials consist of distinguishable areas, substructures, which possess properties of a phase. The areas between the phases, at interfaces cover several unit cells and can possess properties differing from those of the superstructure components. The appearance of a conducting two-dimensional electron gas at the interface between two insulating oxides and appearance of magnetism in a non-magnetic material are merely two among many other examples. A change in the electron orbital occupancy near the interfaces, which is possibly due to charge transfer, is considered to be a key factor responsible for novel properties of superstructural materials.[1] In this regard, investigation of interface properties is one of the most fascinating trends in the physical chemistry of solids.

The behaviour of electrons at the interface layer is presumably governed by electronic reconstruction mechanisms, giving rise to various quantum phenomena.[2, 3] If substructure materials have different electron work functions or chemical potentials, a non-equilibrium state will appear at the interface, and charge will then be transferred until the chemical potential difference disappears. Concurrently, energy band bending takes place and the number of electrons is altered compared to the ground state of the substructures. The charge passing through the interface is such that the resulting electric field in a certain area becomes equivalent to the chemical potential difference between the two materials, thus preventing futher charge transfer.[1, 4, 5]

The properties of inorganic superstructures and composites depend on the properties and dimensional characteristics of the substructures, the feasibility of interaction between the substructures through charge transfer and

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electronic reconstruction of interface atoms, as well as on the architecture and synthesis conditions of the material. At present, this set of parameters has been divided according to the function of the material, their combinations being optimized *via* screening. A considerable number of investigations in the context of searching for new magnetic and superconducting materials have been reported.[1,6–11] For composites, semiconductors and insulators, the interface effects have been comprehensively studied.[2–4,12–14] In some papers, attempts are made to obtain ceramic materials with a desirable combination of electronic and ionic conductivity.[15,16] Integration of such attempts resulted in the creation of a new branch of science — nanoionics, which declares the possibility of increasing ionic conductivity of composites by making use of diffusion transfer by nanoscale distances and amorphous defective structures at interfaces.[17]

It follows from the views of supramolecular chemistry that the interacting substructures must be complementary,[18] and the energy of ion–ion interactions resulting from charge transfer can be consumed either in self-organization of a superstructure[19–22] or in electronic and structural rearrangement of the interfaces. In the case of strong ion–ion interactions, self-organization processes are also possible in the absense of structural or bonding compatibility of substructures, *i.e.*, if they are incommensurate.[19,23,24] The complementarity principle is then seen from a different angle and the stability of superstructures with variable compositions at given conditions (temperature and pressure) should be determined by charge transfer and change in the valence states of atoms at the interface.[20,24] According to the supramolecular model of eutectics, non-equilibrium crystallization conditions enable the existence of metastable structural states, or so-called non-autonomous phases.[25] It has been proved that the emergence of metastable structural states is due to the incommensurability of interacting substructures.[19,23,26,27]

The processes governed by charge transfer at interfaces of inorganic superstructures and composites have not yet been adequately investigated. Some review articles consider the electronic quantum phenomena at complex oxide interfaces and related superconductivity and ferroelectricity,[2,4,9] as well as charge transfer in layered metal chalcogenides known as misfit compounds.[28,29] Within the framework of a superstructure concept, the present review summarizes the theoretical and experimental research results of structural and electronic effects at interfaces of both complex oxides and misfit compounds.

Complex oxides, in particular, perovskites,[4,30,31] can exhibit enhanced or novel properties differing from the properties of individual components, which is due to interface processes, such as electronic reconstruction, atomic intermixing, exchange coupling and finite size effects.[12] The perovskite oxides possess important properties — ferroelectricity, superconductivity and ferromagnetism.[3] Perovskites mostly appear as considerably stable superstructures; their practical applications have been reported in the literature.[28,29] Phase stability of perovskites at a given temperature depends on the partial pressure of oxygen and hence, doping with transition metals during the synthesis is often used to stabilize some perovskites.[31]

Misfit compounds are layered metal chalcogenides $(MX)_n(TX_2)_m$ (M = Sn, Pb, Bi, Sb or Ln, T = Ti, V, Cr, Nb or Ta, X = S, Se).[32,33] The main distinctive feature of such compounds is the incommensurability of MX and TX_2 substructures, which influences the crystal morphology and gives rise to unusual physicochemical properties, non-additive thermodynamic characteristics and multistep phase transitions.[21] Misfit compounds occur in natural minerals — cylindrite, franckeite and others.[23]

II. Experimental investigation of interface junctions

II.1. Oxide superstructures and composites

Complex oxides having a high critical temperature of superconductivity are layered superstructures structurally similar to perovskites (Fig. 1). They often incorporate copper oxide layers located between MO type layers (M is an alkaline earth or rare earth metal). In some superconductors, additional layers like Cu–CuO, TlO, PbO, BiO, *etc.* are also present. Spontaneous charge transfer and strong structural deformations leading to superstructures with incommensurate structural components are sometimes observed in such materials. If these distortions were related to the charge tranfer mechanism, direct quantification of charge transfer by measurement of the deformation would be possible.[35]

Charge transfer within complex oxide interfaces can lead to the appearance of a superconducting state in insulating materials. It has been discovered[1] that at the interface between an insulator, which can acquire superconductivity at a certain temperature, and another material acting as a

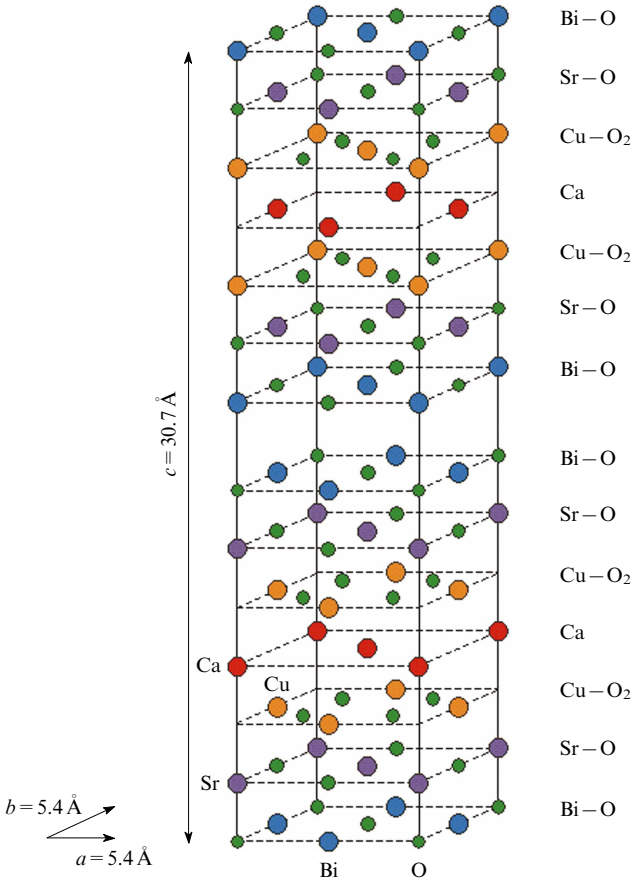


Figure 1. Schematic view of the crystal lattice of the high temperature superconductor $Bi_2Sr_2Ca_1Cu_2O_x$.[34]

charge donor, the insulator can exhibit metallic and even superconducting properties upon accepting electrons. Sm_2CuO_4 and $LaFeO_3$ are both insulators, while Sm_2CuO_4 becomes superconducting when several Sm^{3+} ions have been replaced by Ce^{4+} ions (the electron doped superconductor $Sm_{2-x}Ce_xCuO_4$ is formed). Analysis of X-ray absorption near-edge structure and electron energy loss spectroscopy (EELS) of a $Sm_2CuO_4/LaFeO_3$ superstructure (Fig. 2) grown by high-pressure sputtering onto a substrate in pure oxygen provided evidence for the existence of a metallic state at the interface and an average of 0.09 ± 0.01 e per unit cell charge transfer to the Sm_2CuO_4 d band.

A great number of methods can be used for experimental investigation of charge transfer at the interface of two crystalline compounds with incommensurate structures. For example, an interface between polar $LaAlO_3$ and nonpolar $SrTiO_3$ insulators was prepared using pulsed laser deposition (PLD) on an inert substrate. The optical conductivity of the interface was studied by a combination of high-energy optical reflectivity and spectroscopic ellipsometry.[3] A quasi two-dimensional electron gas was observed at the $LaAlO_3/SrTiO_3$ interface, the appearance of the electron gas depending on the $LaAlO_3$ film thickness. Samples with film thickness of more than 4 unit cells were conductive with charge transfer from $LaAlO_3$ to the interface amounting to 0.5 e. However, samples with $LaAlO_3$ film thickness of less than 3 unit cells were dielectric; in this case, instead of charge transfer to the interface, charge redistribution amounting to ~ 0.5 e was observed within the LaO and AlO_2 substructures of $LaAlO_3$.

The structure of a three-layer $SrTiO_3/LaNiO_3/SrTiO_3$ superstructure grown by PLD in oxygen atmosphere was analyzed by scanning transmission electron microscopy (STEM) and EELS.[14] It was concluded that oxygen vacancies and chemical intermixing play a significant role in polar discontinuity at the $SrTiO_3/LaNiO_3$ interface, which is compensated by lattice dilations and charge transfer. Futhermore, investigation of the charge tranfer between phases in the $LaMnO_3/SrMnO_3$ superstructure by second-harmonic spectroscopy revealed the presence of a unique electronic state, but no metallic conductivity.[36]

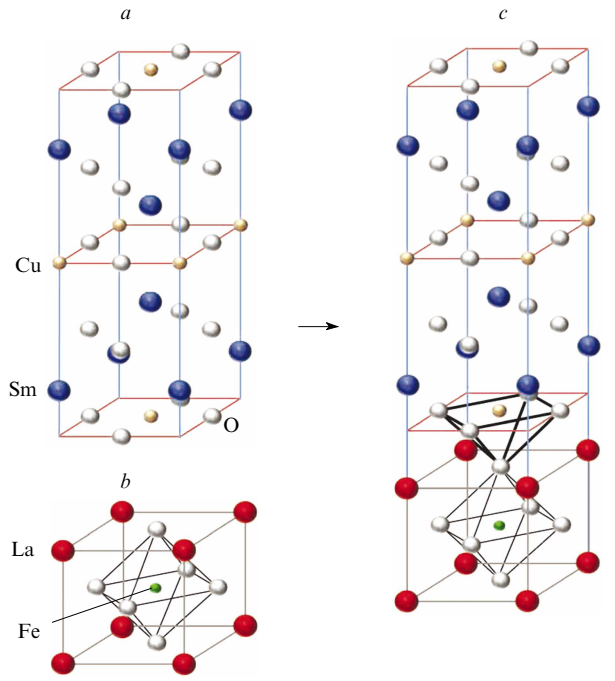


Figure 2. Schematic view of the crystal lattices of Sm_2CuO_4 (*a*), $LaFeO_3$ (*b*) and $Sm_2CuO_4/LaFeO_3$ superstructure (*c*).[1]

The $Bi_2Sr_2CuO_6$ superstructure, a high critical temperature superconductor, has been considered in an early work devoted to the correlation between charge transfer and structural incommensurability.[35] The effect of substructure incommensurability in $Bi_2Sr_2CuO_6$ was detected by X-ray diffraction (XRD). It was hypothesized that any variation of the quantity of the transferred charge results in a structural change. The charge transfer from CuO_2 layers to BiO bilayers in $Bi_2Sr_2CuO_6$ induces a deformation resulting in the localization of carriers; hence, this compound does not possess strong metallic properties. The effect of Sr substitution by different metal atoms — isoelectronic (Ca, Ba) or non-isoelectronic (La, Pr, Bi) ones — has also been discussed for this superstructure.[35] In the case of isoelectronic substitution, a charge equilibrium was retained, and the extent of charge transfer changed only upon changes in interatomic distances caused by differences between the atomic radii. In non-isoelectronic substitution, excess electronic density induced an increase in charge tranfer and strong structural effects, namely, monoclinic-to-orthorhombic phase transition and a substantial variation of the lattice constants.

The existence of a correlation between the incommensurabity of substructures and charge transfer has later been experimentally determined[8] for the $Bi_2Ba_{1.3}K_{0.6}Co_{2.1}O_{7.94}$ superstructure composed of alternating BiO, BaO and CoO_2 layers (Fig. 3). A huge mechanical strain between the layers was shown to induce significant charge transfer (0.6 e per unit cell) from $[BiO/Ba_{0.65}K_{0.3}Co_{0.05}O]$ to the CoO_2 layers. In the authors' opinion, the total energy of the system substantially decreases due to charge transfer, since the electrons pass to a lower-enegry state in the adjacent layer, and the incommensurate superstructure is thus stabilized.

The $Ca_xLa_{1-x}Ba_{1.75-x}La_{0.25+x}Cu_3O_y$ ($0 < x < 0.4$, $6.4 < y < 7.3$) superstructure containing copper oxide layers was prepared by a conventional solid-state synthesis method and analyzed by X-ray absorption spectroscopy and high-resolution powder X-ray diffraction.[37] Excess oxygen atoms, unlike calcium, were found to stimulate the superconductivity by increasing the hole density and the degree of charge transfer. An important conclusion was drawn stating that the phase transition temperature of this compound is controlled by the misfit strain between different layers within the CuO_2 plane rather than by variation of charge density or charge transfer. It was assumed that the incommensurability-induced pressure within the CuO_2 plane exerts a prominent influence on the superconductivity of the system. In other words, the incommensurability-induced pressure is the most probable parameter that determines the critical temperature of phase transition in cuprate families.

The $YBa_2Cu_3O_{7-x}/La_{0.67}Ca_{0.33}MnO_3$ and $YBa_2Cu_3O_{7-x}/PrBa_2Cu_3O_7$ superstructures are ferroelectric/superconductor type systems with 0.5% crystal lattice mismatch. They were grown by high-pressure sputtering on a substrate in oxygen atmosphere and studied by STEM and EELS with a monolayer resolution.[38] Considerable charge

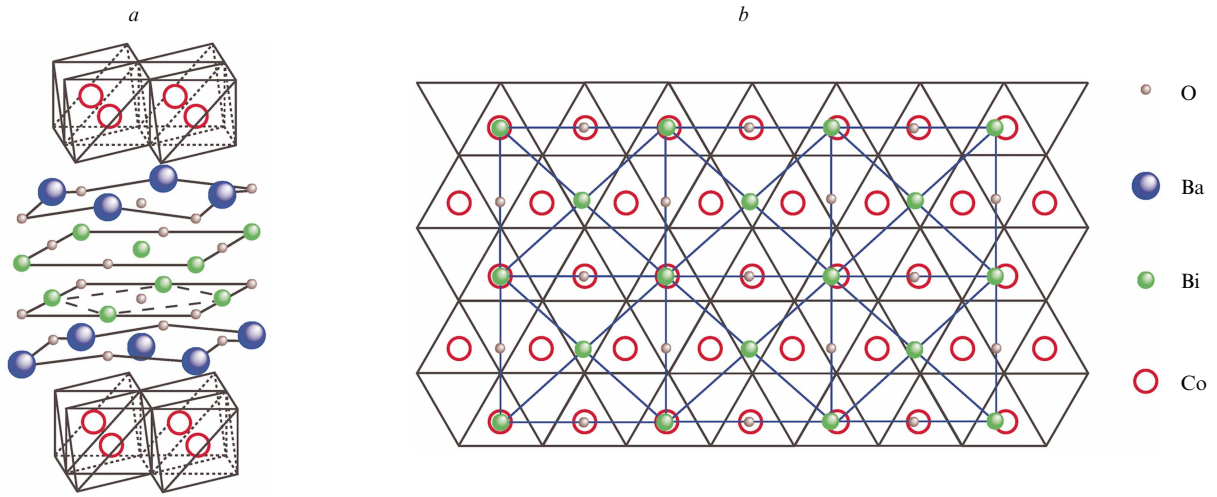


Figure 3. Crystal lattice of $Bi_2Ba_{1.3}K_{0.6}Co_{2.1}O_{7.94}$.[8] (*a*) Side view, (*b*) top view.

transfer from $La_{0.67}Ca_{0.33}MnO_3$ layers to $YBa_2Cu_3O_{7-x}$ layers was observed along with increase of hole concentration in the former. The thicker the $YBa_2Cu_3O_{7-x}$ ferroelectric layer, the greater the charge transfer. As a result, the the $La_{0.67}Ca_{0.33}MnO_3$ substructure contained 0.2 e less per unit cell and the mean oxidation state of manganese atoms was +3.3. It was assumed that the change in the Mn oxidation state in $La_{0.67}Ca_{0.33}MnO_3$ from +3.3 in the terminal layer to +3.5 in the tenth layer from the interface is in good agreement with enhancement of charge transfer between $La_{0.67}Ca_{0.33}MnO_3$ and $YBa_2Cu_3O_{7-x}$ upon increase in the number of layers of the latter.

The situation is different for the $YBa_2Cu_3O_{7-x}/PrBa_2Cu_3O_7$ superlattice. According to the EELS analysis, this system experiences spatial oscillations of hole distribution density with a period equal to the lattice parameter $c = 11.7$ Å, while no energy band bending is observed because Cu atoms are isoelectronic.

Several studies have been devoted to investigation of the interface between a cuprate, $YBa_2Cu_3O_{7-x}$, and a manganite, $La_zCa_yMnO_3$. To obtain the $YBa_2Cu_3O_{7-x}/La_{2/3}Ca_{1/3}MnO_3$ superstructure, two methods were used — high pressure sputtering in oxygen atmosphere and PLD; analyses were performed by cross-sectional scanning tunnelling microscopy and STEM.[13] It was demonstrated by the measurements that the asymmetry of the electronic structure of the interface is coupled with its structural assymetry, and the width of charge transfer region depends on the method of superstructure synthesis.

An experimental study [30] dealing with the same system showed that the lattice defects, such as oxygen vacancies, can play an important role in electronic reconstruction in complex oxides. STEM and EELS examination made it possible to determine finite structures and oxidation states of the interface atoms. The charge redestribution was found to be related to filling of the d orbitals of Mn atoms in manganite layers, which depends on the proximity to the interface. According to the authors electronic structure at the interface is governed by a finite atomic structure. Theoretical modelling of the $YBa_2Cu_3O_{7-x}/La_{2/3}Ca_{1/3}MnO_3$ systems demonstrated [30] that the electronic structure at the interface is formed through an interplay between the charge transfer (strong ionic bonds between the phases) and substitution of copper atoms for manganese within the $La_{2/3}Ca_{1/3}MnO_3$ substructure. It was also observed that the thin substructure layers adjacent to the interface possess higher electron density. This unexpected phenomenon is at strong variance with the conventional physics of semiconductors and indicates the emergence of some additional energy factor competing with charge transfer effects.

A comprehensive study of the charge transfer in the interface space of a composite system of polycrystalline $ZnO/Zn_{1-x}Mg_xO/ZnO$ films, grown on a glass substrate by ultrasonic spray pyrolysis, performed by measuring the electrical and optical properties has been reported.[39] The crystal structure and surface morphology were analyzed by XRD and atomic force microscopy. It was demonstrated that charge transfer in this system depends on ZnO grain size in crystalline films, while doping the ZnO layers with aluminium induces a 1.6 fold increase in the number of charge carriers and the electron mobility within the interface. Taking into consideration the increase in the electron density at the interfaces, which serves as traps for free carriers from the crystallite bulk, the grain size can be the predominant factor behind the electron scattering at the grain boundaries. The specific surface area of grains (hence, the number of electron traps) increases with a decrease in the grain size. However, the grain interfaces can also be filled with electrons, and then a layer depleted of electrons appears at the grain boundaries. The height of the energy barrier for electron mobility, which is related to the depleted layer thickness, is in inverse proportion to the charge carrier density in the grain. Therefore, the carrier density increase in the grain bulk should lead to lowering of the energy barrier for electron mobility at the grain boundaries.

Doping of ZnO layers with aluminium in the $ZnO/Zn_{1-x}Mg_xO/ZnO$ system, even in the case of particularly small-size grains, can lower the energy barrier for electron mobility, so that the mobility and transfer of electrons at the interface are enhanced. Nonetheless, doping with Al cannot provide sufficiently high electron mobility due to intense electron scattering at the grain boundaries. Futher increase in the electron mobility and decrease in the electron scattering are possible through improvement of film crys-

tallinity, *i.e.*, increase in the grain size. Considering the above mentioned effects, enhanced charge transfer in the three-layer $ZnO/Zn_{1-x}Mg_xO/ZnO$ system can result from both doping of the ZnO layer with Al and grain size increase.

II.2. Transition metal chalcogenides

Misfit compounds are layered superstructures of the host–guest type. Their main difference from intercalation compounds is that the guest (pseudocubic chalcogenide MX structure) is incommensurate to the host (layer TX_2 substructure) along one crystallographic direction (Fig. 4).[19, 21, 40, 41] The incommensurability affects the morphology of the crystals, which resemble microscopic rolls of insulating tape with a hollow core and a fixed diameter. It has been demonstrated[19] that this morphology is determined by the incommensurability and interaction potentials of the guest and the host, related to charge transfer from MX to TX_2. Since the guest and host structures are retained in misfit compounds, assigning these compounds to subjects of inorganic supramolecular chemistry is fully justified.

A number of reviews have been devoted to charge transfer and properties of misfit layer superstructures $(MX)_n(TX_2)_m$ ($1.08 < n < 1.23$, $m = 1, 2$),[32, 42, 43] and $(MX)_nTX_2$[32, 44] (M = Sn, Pb, Sb, Bi, Ln; T = Ti, V, Cr, Nb, Ta; X = S, Se). In these papers, the following points have been stated:

— the charge transfer always takes place from MX to TX_2, so the MX layer is the donor and TX_2 is the acceptor of electrons;

— the electronic structure of M atoms must play an important role in layer interaction.

It was reported in a review[33] that the formation of a $(MX)_n(TX_2)_m$ structure devoid of rare earth elements is confined to metals (M) possessing a lone pair of electrons in a bivalent (Sn, Pb) or a trivalent (Sb, Bi) state. In other words, the lone pair of the M atom must be of crucial importance for layer interaction. It has also been proved that the quantity of charge transferred at the interface depends on the M atom nature. In the case of M being a rare earth element and T = Nb, Ta, a significant charge transfer is observed (1.9 e per Nb atom, M = La); if M = Sn, Pb, Bi and T = Nb, Ta, charge transfer is minor, if any. It has been reported[44] that in MX compounds, both bivalent and trivalent rare earth elements occur in the +2 oxidation state, whereas in superstructures, they tend to be stabilized in the +3 oxidation state. This was attributed to electron transfer from the d–f band of the MX layer to the d band of the TX_2 layer, resulting in the formation of so-called macroionic bonds between the layers. A Raman spectroscopy investigation of the charge transfer in the $(MS)_nNbS_2$ (M = Ln) misfit compounds prepared by chemical vapour transport method demonstrated that the charge transfer from MS to NbS_2 is closely related to the valence of the M atoms and is virtually independent of the sort of atoms at a given valence.[45] The results of XRD analysis and resistivity measurements for $(TbS)_{1.21}NbS_2$, $(TbS)_{1.20}TaS_2$, $(DyS)_{1.22}NbS_2$ and $(DyS)_{1.21}TaS_2$ indicated that all these compounds have hole conductivity and that the rare earth elements are trivalent in the MS substructure.[10]

The charge transfer at a trivalent M atom has been interpreted[42] as shown in the following example: Cr^{4+} is unstable when surounded by chalcogen atoms, which rules out the formation of a binary CrS_2 layer structure. However, such a layer is present in compounds of the $ACrS_2$ type, where A = Li, Na is the electron donor and CrS_2 is the electron acceptor. CrS_2 layers are also observed if they alternate with MS (M = Ln) layers. In both cases, Cr^{4+}

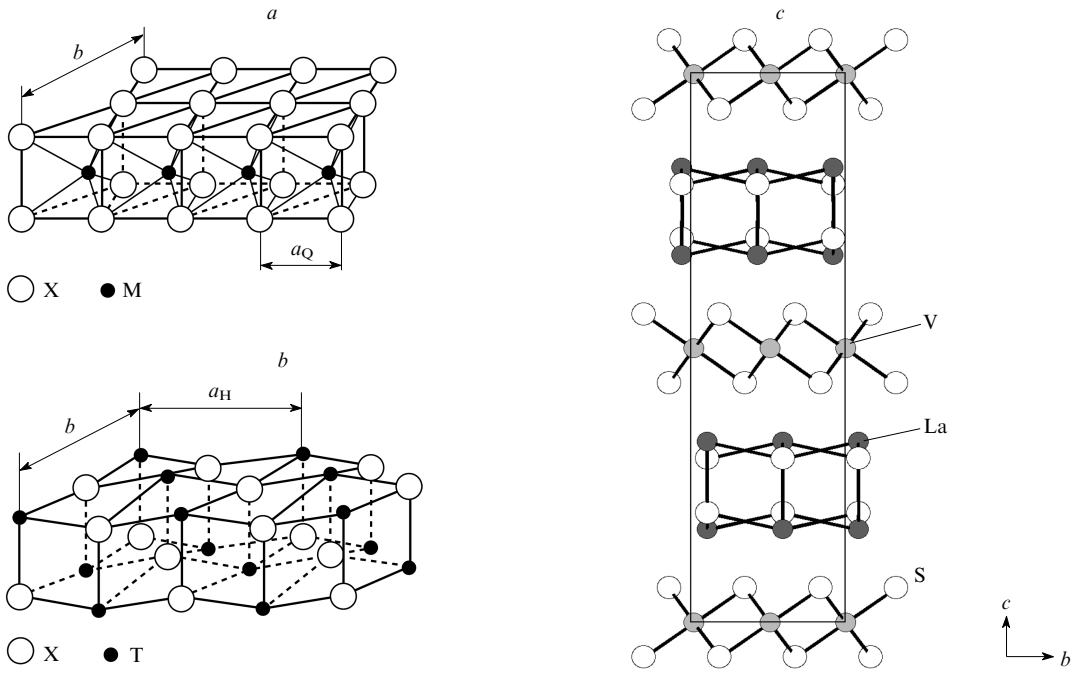


Figure 4. Schematic view of the substructures MX (*a*) and TX_2 (*b*) of incommensurate misfit compounds with lattice parameters a_Q and a_H (see Ref. 19) and the layered structure $(LaS)_{1.18}VS_2$ (*c*).[41]

was reduced to Cr^{3+}, one electron being transferred on each chromium atom. Nevertheless, misfit compounds containing a Cr atom in combination with a divalent M atom are unknown. When divalent M atoms (such as Pb or Sn) were concerned, the charge transfer was doubted. On the contrary, a study applying various spectroscopic methods demonstrated that charge transfer takes place even with divalent M atoms, but to a lesser degree than with trivalent atoms.[32]

The influence of M atom valence on the charge transfer has been confirmed [46] in a paper devoted to investigation of the thermal and electric conductivity in $(MS)_n(TiS_2)_2$ (M = Pb, Bi, Sn) obtained by a solid-liquid-vapour reaction method. The assumption was made that electric conductivity of misfit compounds is determined by the concentration and mobility of charge carriers (electrons). It was dicovered that a high concentration of electrons in $(MS)_n(TiS_2)_2$ is caused by the charge transfer from MS to TiS_2, the charge transfer being 0.45, 0.16 and 0.2 per Ti atom for Bi, Sn and Pb, respectively. Unlike tin and lead, bismuth is trivalent, hence, one electron can pass from the BiS layer to the TiS_2 layer, which is equivalent to 0.6 e per Ti atom and is in good agreement with the value of 0.45 e derived from the experiment. On the contrary, an X-ray photoelectron spectroscopy study of $(SbS)_{1.15}(TiS_2)_m$ ($m = 1, 2$) revealed no charge transfer.[47] Investigation of the compounds $(MS)_nTaS_2$ (M = Pb, Sn or Ln) prepared by the chemical transport method [48] also demonstrated negligible charge transfer for Pb and Sn, while in the case of rare earth elements, it enhanced with increasing atomic mass from La to Gd. It was concluded that the degree of charge transfer in rare earth metal misfits depends on the incommensurability of the substructures.

The stability of $(MX)_n(TX_2)_m$ superstructures is attributed either to charge transfer between the substructures,[42, 44] or to covalent bonding between the layers,[32, 43] or to both these factors along with the posibility of reverse charge transfer from the X atoms of the TX_2 layer to the MX layer.[44] It has been hypothesized [44] that the X atoms of the TX_2 layer involved in the interaction with the MX layer can act as effective scatterers or localization centres for the conduction electrons in the TX_2 layer. Moreover, replacement of the M atoms in MX by the T atoms from TX_2 can be a reason for the stability of misfit compounds. For example, a photoelectron spectroscopy examination of $(PbS)_{1.13}TaS_2$ prepared by chemical vapour transport revealed that the Ta atoms penetrate into the PbS layers and Pb atoms get into the TaS_2 layers, thus readjusting the charge equilibrium.[49] It was suggested that migration of Ta atoms into the PbS substructure results in electron transfer from PbS to TaS_2, so that the alternating PbS and TaS_2 layers are charged and become bound by electrostatic forces. The concentrations found for the substituted atoms vary in the 5% – 20% range, the effective charge transfer from PbS to TaS_2 being 0.1 e per TaS_2 unit cell.

The presence of defects, interdiffusion processes or chemical reactions across the interfaces of semiconductors can exert a substantial effect on their band offset values (Fig. 5). Another possible factor is the existence of quantum dipoles at the interfaces due to local tunnelling of charge carriers through the barriers defined by the band offsets. Photoemission spectroscopy has been used [50] to investigate the quantum dipole phenomenon at the interfaces of incommensurate superstructures composed of epitaxial semiconducting SnS_2 and $SnSe_2$ layers formed on various single-crystalline layered chalcogenide substrates (WSe_2, MoS_2, $MoTe_2$, GaSe). The interfaces of the studied systems were free of structural defects, which are usually present in misfit compounds containing Group III and V or II and VI elements, since they were grown by van der Waals epitaxy on substrates and were composed of alternating X – T – X or X – T – T – X sandwich layers (X is chalcogen, T is metal). The surface of every layer, comprised of chalcogen atoms, was chemically inert; therefore, the interfaces between such layers were considered to be perfect, *i.e.*, involving no change in the crystal structure or strong bond formation. The band bending values for each system determined as functions of the film thickness were slightly different from those calculated according to the electron affinity rule. The discrepancy was attributed to the occurrence of localized quantum dipoles at the interface.

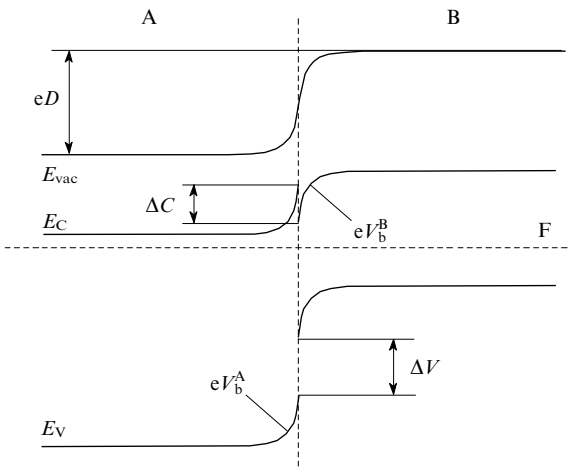


Figure 5. Energy band bending upon contact of two semiconductors with the valence band offset ΔV and conduction band offset ΔC.[50]
eV_b^A and eV_b^B are band bending of substructures A and B, eD is the interface dipole; E_{vac} is the vacuum level; E_V is the upper energy level of the valence band; E_C is the lower energy level of the conduction band.

It is generally known that the TX_2 layer structures can form type II heterojunctions, that is, junctions in which the valence and conduction band offsets have opposite signs.[51] In heterojunctions of this type, the conduction band minimum and the valence band maximum are located in different substructures, thus providing an effective separation of electrons and holes. A layer structure of the ZnS/(CdS/ZnS)$_n$ ($n = 2, 4, 8$) type has recently been synthesized by the PLD method. Its properties were characterized by XRD, STEM coupled with X-ray energy dispersive spectrometry (EDS) and Raman and temperature-dependent photoluminescence spectroscopy.[52] It was assumed that the electron transition from the CdS layer to the holes within the ZnS layer occurs under the action of the excitation energy (Fig. 6). The MoS_2/WS_2 superstructure was studied by photoluminescence and femtosecond pump – probe spectroscopy.[53] It was demonstrated that the transfer of holes from the MoS_2 layer to the WS_2 layer is accomplished within 50 fs after the optical excitation.

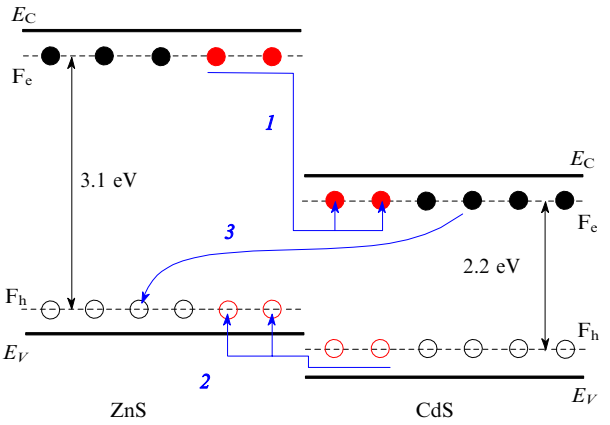


Figure 6. Schematic view of charge transfer at the CdS/ZnS interface.[52]
(*1*) Electrons migrate from the ZnS electron Fermi level to the CdS electron Fermi level; (*2*) holes migrate from the CdS hole Fermi level to the ZnS hole Fermi level; (*3*) charge transfer of CdS electrons to the ZnS holes takes place under the action of excitation energy.
F_h is the hole Fermi level; F_e is the electron Fermi level

III. Theoretical study of interfaces in inorganic composites

Theoretical studies of interfaces in semiconductors and insulators are based on their modelling by quantum chemistry and molecular dynamics methods. An early relevant study [54] was concerned with the charge transfer at the interface between silicon carbide and graphene (referred to as monolayer graphite by the authors). The authors used the cluster calculation method to analyze the charge distribution between the atoms. It was found that charge transfer at the interface depends on the relative positions of carbon atoms in the substructures, the superstructure stabilization resulting from the charge transfer between the incommensurate carbon atoms. In the case of a commensurate arrangement of graphene carbon atoms (Fig. 7) exactly above the silicon atoms of SiC, no charge transfer took place. The incommensurability of the atom positions resulted a relatively pronounced charge transfer from silicon carbide to the graphite monolayer. It was ascertained that in the case of commensurate positions, the 2s and $2p_z$ orbitals of carbon readily overlap with the sp^3 orbital of silicon, whereas in the incommensurate arrangement, the valence sp^2 orbitals of carbon are delocalized and, hence, the carbon and silicon orbitals overlap to a larger extent, resulting in an increase in the s orbital component.

Calculations of the binding energy between alternating two-dimensional layers of MoS_2 and germanene (a germanium monolayer) or silicene (a silicon monolayer) demonstrated that interlayer interactions are stronger in the germanene/MoS_2 system than in the silicene/MoS_2 system, in which the interaction is, in turn, stronger than in the graphene/MoS_2 system.[55] It was also demonstrated that the charge transfer between the layers is more pronounced in the germanene or silicene systems compared with the graphene system. Futhermore, the lattice relaxation times for these composites are different, pointing to a correlation between the charge transfer and the lattice incommensurability. It was discovered that in the germanene/MoS_2

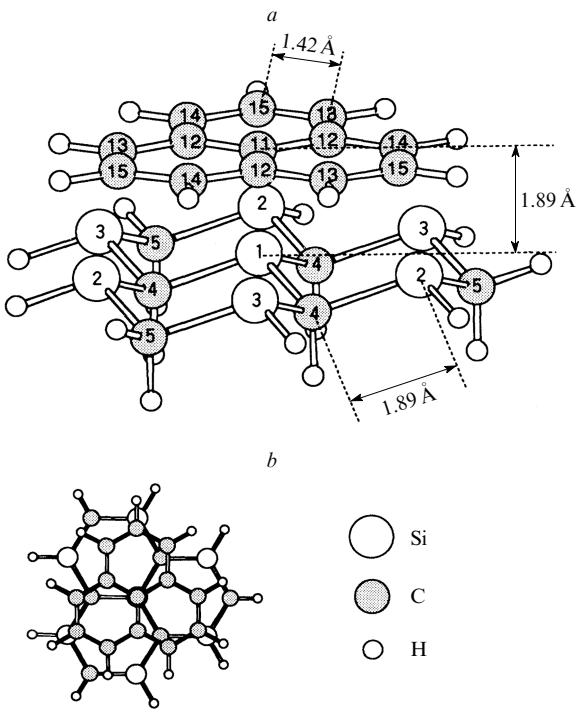


Figure 7. Schematic structure of the graphite monolayer/silicon carbide model cluster ($C_{13}H_9/Si_7C_6H_{15}$). The C(11) atom is located in a commensurate position, *i.e.*, directly above the Si(1) atom.[54]
(*a*) Side view; (*b*) top view.

superstructure, the germanene layers are compressed by 0.47%, while the MoS_2 layeres are expanded by 0.22% as compared with the free-standing layers. In the silicene/MoS_2 superstructure, the silicene layers are expanded by 2.26%, while the MoS_2 layers are compessed by 1.29%. It can be concluded from these data that an increase in the incommensurability depresses the charge transfer and interlayer substructure interaction. Moreover, according to the band structure calculations, the considered superstructures behave as metals.

The calculated values of charge transfer vary for different superstructures. In SnS/SnS_2, the charge transfer from sulfur of the SnS_2 layer to tin of the SnS layer was ~0.1 e per SnS_2 unit cell.[43] These values were ~0.4 e per Nb atom for $(SnS)_nNbS_2$;[56] 0.2 e per Ti atom for $(SnS)_{1.20}TiS_2$;[57] 1.2 e per Cr atom for $(LaS)_{1.20}CrS_2$;[58] and 0.7 e per Nb atom for $(LaS)_{1.14}NbS_2$.[59] The charge transfer from the LaS layer to the CrS_2 layer in $(LaS)(SrS)_{0.2}CrS_2$ was 1 e.[41] In a number of theoretical studies,[41, 56–58] it has been shown that the energy band structure of the interfaces in misfit compounds can be approximated as a superposition of the energy bands of the two substructures. Energy band dispersion of superstructures indicates that a significant covalent bonding occurs between the M atoms of the MX substructure and the X atoms of the TX_2 substructure across the interface, whereas the contribution of electrostatic interactions due to charge transfer is notably smaller.

Stabilization mechanisms of the compounds $(PbS)_{1.8}TiS_2$ and $(PbS)_{1.8}(TiS_2)_2$ have been studied by calculations of the band structure and the electron density-of-states function.[60] The calculated values were compared with experimental data obtained by transmission electron dif-

fraction and high-resolution transmission electron microscopy coupled with EDS. The authors concluded that in misfit superstructures, unlike their constituent components, a p – d band is opened and the conduction band is filled with electrons. A theoretical investigation of the stabilization of the compound $(PbS)_{1.14}TaS_2$ has been reported.[61] It was found by calculation of the electron density-of-states function that the dominating stabilization mechanism in this system is non-stoichiometric, *i.e.*, Ta atoms are substituted for the Pb atoms within the PbS structure. When the substitution concentration equals $\sim 0.13 - 0.19$, the PbS and TaS_2 substructures should be stabilized. According to the calculations, stabilization is provided by the charge transfer from PbS to TaS_2.

In accordance with the theoretical estimates, the layered composites can exhibit metallic behaviour even if the components are good insulators. It has been reported [62] that in a nanostructured multilayer insulator system, the electrons can be redistributed across the whole structure, which thus acquires metallic properties. Charge transfer modelling for a $KTaO_3/SrTiO_3$ superstructure has also revealed [63] that a metallic state is formed at the junction between $KTaO_3$ and $SrTiO_3$ insulators. The existence of such state is explained by weakening of the bond between the transition metal and oxygen atoms and the change in their orbital occupancy. Futhermore, it was suggested that the minimum incommensurability of $KTaO_3$ and $SrTiO_3$ substructures results in formation of a chemical bond across the interface and the charge transfer between the phases is then confined to a very thin (~ 12 Å) layer.

It is well known that perovskites based on manganese oxides $La_{1-x}Sr_xMnO_3$ change their properties depending on the x value. For example, $La_{0.67}Sr_{0.33}MnO_3$ and $La_{0.33}Sr_{0.67}MnO_3$ perovskites are composed of $LaMnO_3$ and $SrMnO_3$ layers, yet the former is a ferromagnet and the latter is an insulator. In such systems, the charge transfer and existence of the metallic state at the interface are governed by substructure layer thickness, and with an increase in the substructure layer thickness, its properties gradually approach those of the free components.[64]

In another theoretical investigation devoted to $(LaMnO_3)_m/(LaNiO_3)_n$ ($2 \leqslant m \leqslant 3$ and $2 \leqslant n \leqslant 4$) composites,[65] the electron transfer from Mn to Ni was shown to enhance with increasing m/n ratio, or, in other words, to depend on the relative thickness of the substructure layers. In the modelling of $(LaMnO_3)_{2n}/(SrMnO_3)_n$ ($n = 1 - 4$) superstructures, a metal-to-insulator transition at the interface with increasing n was observed.[66]

IV. Conclusion

Analysis of the accumulated data in the field of inorganic superstructures and composites showed that their interface properties depend on the difference between the chemical potentials of interacting substructures, their electronic structures, incommensurability of structural parameters as well as conduction properties. This influences the distribution of energy obtained by the superstructure as a result of charge transfer. The bulk properties of composite materials may be directly determined by the energy of non-covalent interactions between the substructures, as well as the proportion of interfaces in their bulk. One can also assume that the properties of composite materials are largely dependent on the methods of their preparation and nanostructuring.

The electronic structure of interfaces is closely related to the geometry and chemical composition of the superstructures. A metallic state within the interfaces of a number of layered superstructures and composites, including both complex oxides and chalcogenides, can emerge due to electron transfer, even if free substructure substances are insulators. However, the possible absence of a metallic state at an interface is related to the substructure layer thickness and nature of the constituent metals. The layer thickness of the interacting substructures should have a certain optimum value: too thin layers lead to a change in their properties, while excessively thick layers bring about properties of individual components (substructures).

For misfit compounds, it has been found that the valence and the chemical nature of the metal M govern the extent of charge transfer from the MX to the TX_2 layers. In the case of a trivalent metal, the charge transfer is pronounced, whereas with a bivalent metal, it may not even be observable.

Stabilization of superstructures occurs as a result of both electron and metal atom transition from one substructure into the other one, in addition to possible covalent bond formation between the layers. The interaction of substructures is dependent on their lattice incommensurability (mismatch) value. The charge transfer and the incommensurability influence each other. For one, spontaneous charge transfer can result in substructure lattice deformations, phase transitions and formation of incommensurate superstructures. And *vice versa*, mechanical strain between the layers caused by incommensurability of the substructures can give rise to charge transfer at the interface. Nevertheless, with increasing incommensurability, the charge transfer and interactions between the layers are reduced.

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