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On matrix stabilisation of d- and f-transition metal ions in unstable oxidation states

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Abstract. The state-of-the-art in matrix stabilisation of d- and f-transition metal ions in unstable oxidation states is analysed. Main aspects of this problem concerning the genealogy of appropriate matrix systems are classified. Relevant examples are given and the data that contradict the scheme proposed are discussed. The thermodynamics of the matrix stabilisation effect is considered using the concept of isomorphic miscibility. The influence of defects and non-equilibrium on the matrix stabilisation effect is discussed. The problem of identification of the oxidation states in matrix systems is examined and various types of matrix systems are considered. The bibliography includes 174 references.

I. Introduction

Doping is a well-known technique for modifying the properties of various compounds and materials. Introduction of impurity ions (dopants) into solid compounds (matrices) leads to changes in the properties of the systems thus formed compared to the properties of the undoped compounds.† Doping is widely used in practice to modify the chemical, physical and mechanical properties of various materials. Restricting ourselves to chemical manifestations of the doping effect, mention should be made of a vast variety of systems. For instance, the number of only paramagnetic compounds much exceeds a value of 1000 (results obtained for these matrix systems are summarised in Ref. 1). Doping of semiconductor materials (in particular, solid solutions based on lead telluride[2]) with impurities (including metal ions) was also reported. Recently, doping in studies of high-temperature superconductors (HTSC), manganites and other novel materials has been topical; there is considerable literature on the subject. A large review[3] is devoted to the theory and applications of HTSC. The authors of a fundamental review[4] considered the chemical principles of preparation of metal-oxide semiconductors and, in particular, paid attention to the important role of ionic doping of appropriate matrices to attain the high-temperature superconductivity effect. The key properties of HTSC and details of the superconducting and magnetic phase diagrams of the best studied HTSC $La_{2-x}M_xCuO_4$ (M = Ba, Sr) have been reviewed.[5] Problems in physics of high-temperature superconductors have also been considered from the standpoint of doping of Mott insulators.[6] This model, which became the starting point in analysing the electronic structure of oxocuprates, is based on the concept of strong correlations. The authors of review[6] used Anderson's idea of 'resonant' charge states[7] and proposed new approaches to establishment of the nature of oxide HTSC.

These and other typical fundamental studies have been focussed on applied problems of doping. This is also characteristic of communications reported by other researchers, in particular, geochemists and crystal chemists.[8] For instance, matrix systems have long been used for preparation of laser crystals containing transition-metal impurity ions (see, *e.g.*, Refs 9 and 10). The role of matrices can be played by crystalline fluorides (CaF_2, LaF_3, $LiYF_4$, *etc.*), oxides (*e.g.*, corundum α-Al_2O_3) or complex compounds, such as scheelite $CaWO_4$, aluminium yttrium garnet $Y_3Al_5O_{12}$, apatite $Ca_5(PO_4)_3F$, *etc.*; laser materials $Y_3Al_5O_{12}$:Nd^{III}, $Y_3Al_5O_{12}$:Yb^{III} (see Refs 11 – 13), CaF_2:$Yb^{II/III}$ (see Ref. 14) are also known. Laser matrix crystals can be doped with other lanthanide ions (Pr^{III},

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† Matrix systems are in essence limited solid solutions and can be described using corresponding thermodynamic formalism.

Nd^{III}, Er^{III}, Ho^{III}, Tm^{III}) and with some transition metal ions (Cr^{III}, Ni^{II}, Co^{III}, V^{II}). Matrix systems containing Sm^{II}, Dy^{II}, Tm^{II}, *etc*. used as laser materials,[15–17] as well as IR-sensitive luminophores based on CaS, SrS and BaS containing immobilised $Eu^{II/III}$, $Sm^{II/III}$, $Tb^{III/IV}$, $Ce^{III/IV}$, *etc*. ions (see, *e.g*., Refs 18 and 19) are of interest. Doping allows the colour of compounds and minerals to be changed for various practical purposes. This effect can be illustrated taking the Cr^{III} ions occupying sites of different local symmetry in the matrix lattice as examples. For instance, the system α-$Al_2^{III}O_3$:Cr^{III} is red, $Al_2^{III}Be_3Si_6O_{18}$:Cr^{III} ($Al_2Be_3Si_6O_{18}$ is beryl) is green and the system $Al_2^{III}SiO_5$:Cr^{III} (Al_2SiO_5 is kyanite) is blue.[20,21] The problem of shift of bands in the absorption spectra along the energy axis is topical because of its practical value.[22] Yet another practically interesting problem is to prepare silver halide nanocrystals in alkali metal halide matrices (in particular, AgCl in KCl) when growing crystals with high concentration of Ag^{I} impurity; here AgCl nanocrystals can be treated as quantum dots (see Ref. 23 and references cited therein).

Many other examples of matrix systems suitable for practical applications are available. Note that in most systems used in practice and studied by researchers the dopant ions are in conventional and low oxidation states.

Recently, the so-called matrix stabilisation of unstable oxidation states of elements has been developed.[24,25] The technique involves the introduction of guest metal ions into a crystalline matrix in order to attain a desired oxidation state of the dopant ions; in addition, the matrix should favour extension of the lifetime of this state over a time interval sufficient for identification and use. These assumptions are based on the experimental results. Namely, numerous examples of realisation of this effect have been reported, although often such matrix systems are prepared to achieve a practically valuable effect rather than to stabilise the dopant ion in a given oxidation state. Most researchers ignore the problem of the lifetime of impurity ions in matrix systems, although this parameter characterises the efficiency of stabilisation. This is probably due to the fact that in most cases the metal ions are in conventional oxidation states (for corresponding classification, see Refs 26 and 27).

We use the term 'matrix stabilisation' since 1990.‡ Initially, it was assumed that an impurity ion replaces the host (matrix) ion in the crystal lattice site. However, we believe that this interpretation of replacement is only a possible particular case. The key point is that the process results in stabilisation of the oxidation state of the impurity ion over at least a period sufficient for identification and subsequent use, irrespective of the ion position in the matrix structure.

The aim of this review is to consider the state-of-the-art in the field of matrix stabilisation of transition metal ions in unstable and unusual oxidation states.

This problem is topical for inorganic chemistry and materials science. Here we present experimental data on stabilisation of unusual oxidation states of transition metal ions in solid matrices (Section II) and consider thermodynamic aspects of matrix stabilisation (Section III). We will discuss the size effects and some aspects of the theory of isomorphous miscibility, and the problem of Coulomb potentials existing in the solid phase. Then we briefly outline the formation of point and extended defects (Section IV) and the problem of non-equilibrium; here we will put forward some assumptions concerning the mechanism of matrix stabilisation (Section V). Next, we present a short consideration of the problem of identification of the oxidation states in matrix systems (Section VI), a classification of matrices suitable for stabilisation of unstable oxidation states (Section VII) and, finally, consider methods of preparation of matrix systems containing transition metal impurity ions in unstable oxidation states (Section VIII). The emphasis is placed on the systems containing impurity metal ions in unusually high oxidation states, although ions in low oxidation states were also considered to complete the picture.

II. Experimental data

To synthesise novel compounds and prepare materials based on them, it is important to account for chemical aspects of matrix synthesis. We believe that the key issue in considering stabilisation is the effect of matrix on the oxidation state of the impurity ion. There are at least three main aspects of this problem, which concern the genealogy of matrix systems.

1. The formation of systems can occur under such conditions where the dopant ion in the desired unstable oxidation state already exists and the matrix crystal only stabilises it under the operating conditions. For instance, co-crystallisation of potassium chromate or sulfate with potassium ferrate(VI) from solutions at temperatures $\leqslant 20$ °C resulted in systems (including single-crystalline ones) containing unstable Fe^{VI} ion,§ namely, K_2CrO_4:Fe^{VI} and $K_2S^{VI}O_4$:Fe^{VI} (see Refs 10, 28 and 29). This can be considered as isovalent replacement. Crystals thus formed are thought to be promising optical emission materials. Crystals Cs_2ZrCl_6:Os^{IV}, Cs_2ZrBr_6:Os^{IV} and Cs_2ZrCl_6:Re^{IV} were prepared from melt (~ 500 °C), because the impurity ions, Os^{IV} and Re^{IV}, are more stable than Fe^{VI} (Refs 30, 31).

2. Matrices formed in the course of synthesis can stabilise high oxidation states of dopants, which are not detected in the initial reaction mixtures. For instance, perovskite-like matrices $BaM^{IV}O_3$ (M = Ce, Th, Zr) appeared to be suitable for stabilisation of Pr^{IV}, Tb^{IV}, Nd^{IV} and Dy^{IV} ions. These systems are prepared by the reaction of BaO (or BaO_2) with metal dioxides that form the matrix (M = Ce, Th, Zr) and with dopant-metal sesquioxides in oxygen atmosphere (~ 1000 °C) at dopant ion concentrations of ~ 2 mass % – 16 mass %.[32–34] The system $Sr_2Pb^{IV}O_4$:Pr^{IV} was prepared in a similar manner.[35] Individual phases $BaCe^{IV}O_3$:Pr^{IV}, $BaCe^{IV}O_3$:Tb^{IV}, $BaTh^{IV}O_3$:Pr^{IV}, $BaZr^{IV}O_3$:Pr^{IV}, $BaZr^{IV}O_3$:Nd^{IV}, $BaZr^{IV}O_3$:Tb^{IV} and $Sr_2Pb^{IV}O_4$:Pr^{IV} thus obtained contain Ln^{IV} ions, which are unstable in solution.[32–35] In particular, the lifetime of Pr^{IV} aqua ion is ~ 200 ns,[36] whereas the matrix systems $BaCe^{IV}O_3$:Pr^{IV} and $Sr_2Pb^{IV}O_4$:Pr^{IV} have infinitely long lifetimes under normal conditions.

3. The oxidation state of dopant ions incorporated into matrix crystals can change upon some treatment *in situ*. For instance, changes in the charge state of cerium ions under oxidation or reduction conditions (on heating) in the matrix system ZrO_2:Ce cause the colour of this system to vary from

‡ It was introduced by N S Kopelev, Yu M Kiselev and Yu D Perfilyev (Lomonosov Readings, M V Lomonosov Moscow State University, 1990).

§ It can undergo a rapid transformation to Fe^{III} in aqueous solution even at room temperature.

bright red-Burgundy ($Ce^{III} + Ce^{IV}$) and yellow-orange (Ce^{IV}) to violet or colourless (Ce^{III}) (see a monograph [37]) (isovalent and heterovalent replacement). Highly disperse powders of citrate complexes of Mo^{VI} turn blue after UV irradiation,[38] which indicates the appearance of a paramagnetic impurity (Mo^{V}) in the samples. Specific colour of amethyst (iron-doped quartz) is due to the change in the oxidation state of the iron impurity ions from Fe^{III} to Fe^{IV} upon γ-irradiation.[39] Treatment of CaF_2, BaF_2 and SrF_2 matrices under reduction conditions permits stabilisation of Es^{II} ion.[40] Under particular conditions, Am^{III}, Cm^{III}, Tb^{III} and Pr^{III} ions immobilised in niobates and tantalates can be oxidised ($M^{III} \rightarrow M^{IV}$) and then form corresponding substitution products.[41,42] The CaF_2 lattice is suitable for stabilisation of U^{III} and U^{IV} ions.[17] Some ions, including d-transition metal ions in low oxidation states, are relatively stable in oxide glasses.[43]

The list of examples is not restricted to those given above. Relatively unstable Mn^{III} (Ref. 10), Cr^{IV} and Cr^{V} ions can be stabilised in matrices of garnets synthesised on heating in the solid phase and in chromates and sulfates obtained from solutions. Tb^{IV} ions are stabilised in ($SrMgF_4 : Tb^{IV}$)-phosphors obtained in the solid phase in the presence of molecular fluorine.[44] Finely disperse, X-ray amorphous V_2O_5:Fe^{V} samples were synthesised by heating V_2O_5 and Fe_2O_3 to $\sim$600 °C followed by efficient quenching. The consequences of disproportionation of Fe^{III} ions in these samples were observed by Mössbauer spectroscopy.[45]

Studies of oxide matrix systems based on $M^{I}_2FeO_4$ and $M^{I}_3(Ru^{VI}_{1/2}Ru^{VII}_{1/2}O_4)$ (M^{I} = K, Cs) made it possible to establish [46–48] the conditions for their doping with Co^{n+} and Fe^{n+} ions (oxidation states were identified by ^{57}Fe and ^{57}Co Mössbauer emission and absorption spectroscopies). Among the most interesting results, mention may be made of the stabilisation of Co^{VI} ions in ferrite $Cs_2Fe^{VI}O_4$ (identification by Mössbauer emission spectroscopy).[46,47] The system $Cs_2Fe^{VI}O_4$:Co^{VI} is formed in the solid-phase reaction of CsO_2 with ^{57}Co-doped Fe_2O_3 at 400 °C (Fig. 1).

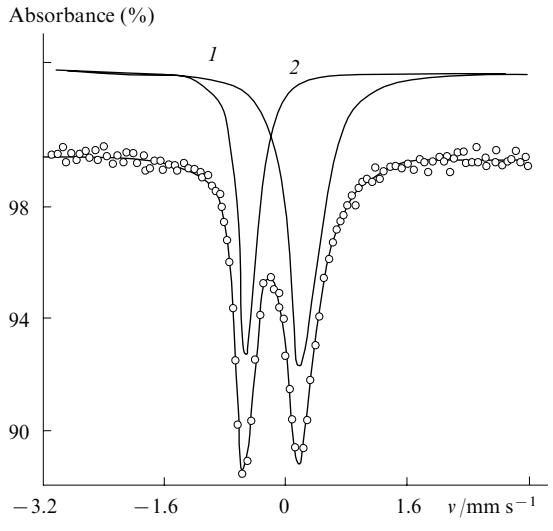


Figure 1. Mössbauer emission spectrum of matrix system $Cs_2Fe^{VI}O_4$:^{57}Co (77 K).[44]
Signals from Co^{VI} (*1*) and Co^{IV} (*2*). The Mössbauer absorption spectrum of the same sample exhibits only a singlet line corresponding to Fe^{VI}. Here and in other Mössbauer spectra the points denote experimental data and v is the source velocity.

Since a small amount of Co^{VI} impurity ions is stabilised in the ferrate(VI) lattice, in this case one probably deals with microisomorphism. Doping of manganate $K_3Mn^{V}O_4$ with ^{57}Fe results in a matrix system K_3MnO_4:Fe^{V} (sintering of KO_2 with ^{57}Fe-doped MnO_2).[48] Fe^{V} ions were also stabilised in an X-ray amorphous glassy matrix prepared by sintering KO_2 with MnO_2 at 800 °C, and the dynamics of Fe^{V} degradation was monitored.[49] Fe^{VI} ions were found in ^{57}Fe-doped oxoruthenate K_2RuO_4 synthesised by heating $KO_2 - RuO_2$ mixtures in the presence of highly disperse $^{57}Fe_2O_3$ (Fig. 2).[50]

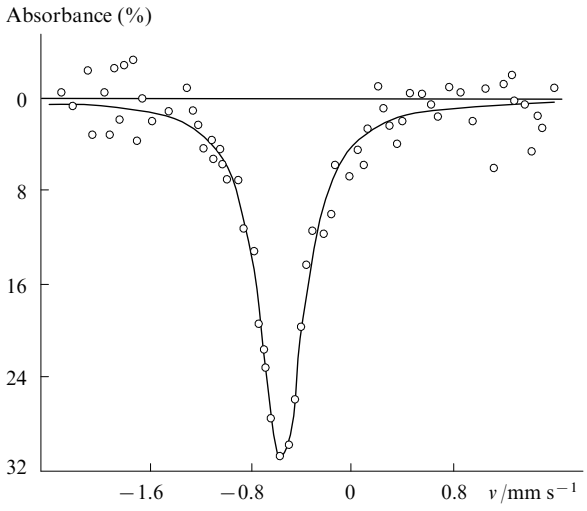


Figure 2. Mössbauer absorption spectrum of system $K_2Ru^{VI}O_4$: $^{57}Fe^{VI}$ (77 K).[50]
Found: $\delta = -0.59$ mm s^{-1}, the expected value for Fe^{VI} is $\delta \approx -0.77$ mm s^{-1}. The chemical shifts (δ) are given relative to sodium nitroprusside.

Since the oxidation states Fe^{VIII} and Fe^{VI} are known, it is interesting to attain the oxidation state Fe^{VII} (generation of charge carriers and the reverse process should necessary occur with the formation of intermediate one-electron states, because any boson field can change the state of only one fermion per act). To stabilise this oxidation state, ^{57}Fe was introsuced into the $Cs_3(Ru^{VI}_{1/2}Ru^{VII}_{1/2}O_4)$ matrix.[51–53] To this end, a mixture of CsO_2, RuO_2 and Fe_2O_3 was sintered at a moderate temperature, which resulted in $Cs_3(Ru^{VI}_{1/2}Ru^{VII}_{1/2}O_4)$:$Fe^{VI}$. In this system the iron ion is mainly stabilised in the Fe^{VI} form. At the same time the Mössbauer spectrum exhibits an unstable satellite shoulder in the wing of an intense singlet from Fe^{VI} (Fig. 3); the chemical shift of this shoulder is close to that expected for Fe^{VII} (assuming the existence of a fluctuating state containing both Fe^{VI} and Fe^{VII}). Unfortunately, no more convincing proofs of the existence of Fe^{VII} in this system are available so far.

According to Mössbauer spectroscopy data obtained at 4 K,[54–56] Fe^{VII} as well as Fe^{VIII} (Ref. 57) ions were also detected in the matrix system Na – Fe – O at a Na : Fe molar ratio of $\gg 50:1$ (Fig. 4). At smaller ratios, a Fe^{IV} compound characterised by unusually high electric field gradient (Fig. 5) is formed.[58] The matrix systems Na_2O_2:Co^{VI} and Na_2O_2:Co^{IV} were prepared by heating ^{57}Co impurity with a large excess of sodium peroxide.[59]

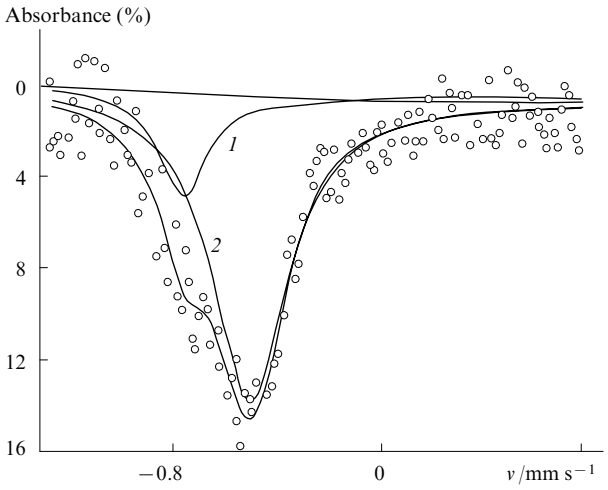


Figure 3. Mössbauer absorption spectrum of system $Cs_3(Ru^{VI}_{1/2}Ru^{VII}_{1/2}O_4)$:^{57}Fe (77 K).[52]
Signal *1* corresponds to $\delta_1 \approx -0.77$ mm s^{-1}; signal *2* corresponds to $\delta_2 = -0.57$ mm s^{-1}; the expected value for Fe^{VII} is $\delta < -0.63$ mm s^{-1}. The chemical shifts are given relative to sodium nitroprusside.

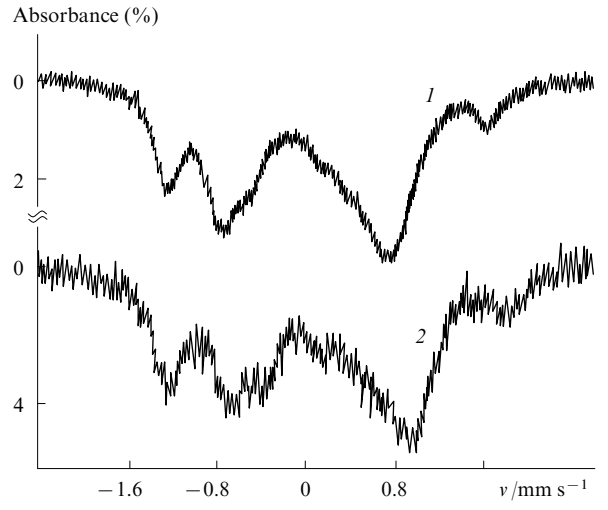


Figure 4. Mössbauer absorption spectra of sintering products of $^{57}Fe_2O_3$ and Na_2O_2.[55,56]
Molar ratio Na : Fe ≈ 100 : 1. The spectra were recorded at 291 (*1*) and 4 K (*2*).

Noteworthy is the possibility for different-valence ions to co-exist in various metal compounds; here, instability of a particular oxidation state leads to detection of a rather low ($\ll 1\%$) concentration of this state (microisomorphism). This first of all concerns radioactive decay products immobilised in the crystal lattice. For instance, the formation of $^{191}Os^{VIII}O_4$:$^{191}Ir^{IX}O_4^+$ was observed in $^{191}OsO_4$ crystals containing a short-lived ^{191}Os isotope.[60] Cm^{V}, Cm^{VI} and Cf^{V} were stabilised in matrices of americium and berkelium compounds in the form of $Cm^{VI}O_2^{2+}$, $Cm^{V}O_2^+$ (see Ref. 61) and $Cf^{V}O_2^+$ ions.[62] In these systems, unstable oxidation states of curium and californium are first of all due to the metal–oxygen bonds.

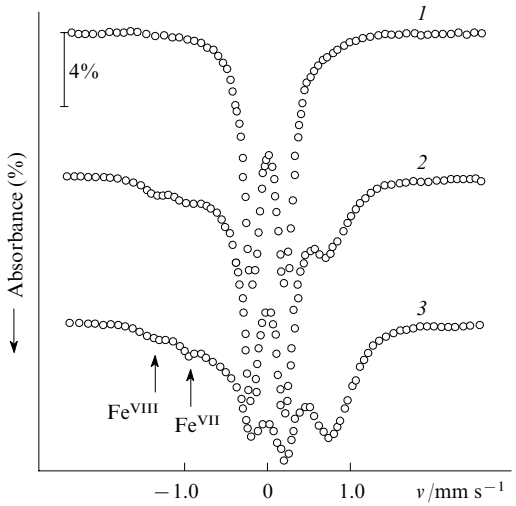


Figure 5. Mössbauer absorption spectra of sintering product of $^{57}Fe_2O_3$ and Na_2O_2 (molar ratio Na : Fe ≈ 40 : 1, 77 K) (*1*) and the spectra of disproportionation products of the sintering product at different instants (*2*, *3*).[58]
Arrows denote the lines, which were tentatively assigned to corresponding disproportionation products; however, correct conclusions about the formation of such derivatives are impossible due to low intensities of these signals.

Unusual external conditions, in particular, low temperatures or high pressures, can also be used to meet the condition $\Delta_r G < 0$ in practice.

For instance, an interesting IR spectroscopic identification of HgF_4 obtained by direct fluorination of mercury and isolated in the solid neon and argon matrices has been reported in the year 2007.[63] The authors of Ref. 63 believed that weak vibrational bands observed in the IR spectra could correspond to a certain normal vibration of the $Hg^{IV}-F$ bond in square HgF_4.¶ At the same time the possibility for the oxidation state Hg^{IV} to exist casts little doubt, because our previous quantum chemical study[64] revealed a shallow minimum on the potential surface even for the neutral and, undoubtedly, unstable molecule HgO_4.[64]

In typical conditions (*e.g.*, a frozen solvent as the matrix), small clusters containing metal ions in unstable oxidation states, in particular, short-lived metal ions with filled inner d-shell and a single valence s-electron in the outer atomic orbital [Zn^{I}, Cd^{I}, Hg^{I}, In^{II}, Ga^{II} and Tl^{II} ($d^{10}s^1$)] are formed.[65–67] These ions were produced by pulsed radiolysis of frozen aqueous solutions using fast optical detection. The reducing agents were a hydrated electron and protons (reduction potentials −2.7 and −2.3 V, respectively). Systems containing low concentrations of Cu^{III}, Ag^{II}, Pb^{III} and Pd^{III} ions were prepared[65] under appropriate conditions (hydroxyl radical as oxidising agent; oxidation potential ~2.9 V). Clusters containing

¶ IR spectrum of this fluoride was recorded under matrix isolation conditions against the background of the spectra of HgF_2 and its oligomers. Although the authors of Ref. 63 reported rather strong arguments (including results of quantum chemical studies) in favour of the existence of HgF_4, there is a nonzero probability that the observed very weak absorption band is due to a square fragment of polymeric HgF_2.

silver ions in unstable oxidation states have been studied in detail.[65,68–71] Investigations of systems containing metals in different oxidation states are of great importance for the development of theory of photographic process.

Small clusters containing metal ions in unstable oxidation states can also form in the course of synthesis of solid compounds under conventional conditions. For instance, the synthesis of normal alkali metal molybdates in the reactions of MoO_3 with alkali metal superoxides (KO_2, CsO_2) at moderate temperatures ($\leqslant 600\ ^\circ C$) is accompanied, according to EPR data, by the formation of small amounts of molybdenum bronzes responsible for the presence of paramagnetic clusters containing Mo^V in the normal molybdates.[72,73] Meanwhile, the formation of dopant ion aggregates (or clusters) in matrix systems has been known and studied for some time. For instance, cluster fragments $\langle Ln_6F_{37}\rangle$, $\langle Ln_5F_{36}\rangle$, $\langle Ln_4F_{36}\rangle$ were found in mixed crystals $(M^{II}F_2)_{1-x}(LnF_3)_x$ (M = Ca, Sr, Ba, Ln = La to Lu, Y).[74–76]

The problem of matrix stabilisation of unusual oxidation states is directly related to the thermodynamics of formation of matrix systems.

III. Thermodynamics of matrix stabilisation

1. Size effects and theory of isomorphous miscibility

Consider replacement of metal ions occupying lattice sites in the host matrix by impurity ions. Replacement in homodesmic (cage) structures is illustrated in Fig. 6. The structure of compounds is often discussed using such parameters as the ionic radii. In fact, the case in point are the equilibrium metal–ligand distances in the nearest coordination environment, determined from structural data. In other words, this implicitly assumes a thermodynamic description of the solid system. Indeed, the newly formed system is already in at least a quasi-equilibrium state, because the formation of rigid crystal lattice hinders any motions (except thermal vibrations) of the constituent ions.

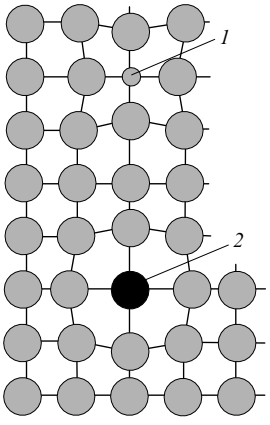


Figure 6. Replacement of atoms occupying lattice sites (homodesmic crystal).
Lattice shrinkage (*1*) and expansion (*2*) on replacement by small and large atoms, respectively.

The importance of the size factor follows from the theory of isomorphous miscibility,[77] which is conventionally used to describe the matrix stabilisation effects in the case of isovalent isomorphism (see †).[24,78] The main equation of this theory for the enthalpy of mixing (ΔH) has the form:

$$\Delta H = x_1x_2\left[\left(\frac{A}{R}\right)(\varepsilon_1-\varepsilon_2)^2 + cmn\, z_M z_X \left(\frac{\Delta R}{R}\right)^2\right] = \quad (1)$$

$$= 332\, m z_M z_X x_1 x_2 \left[\alpha\frac{(\Delta\varepsilon)^2}{2R} + c' n\left(\frac{\Delta R}{R}\right)^2\right],$$

where x_i are the mole fractions of components i; A is the Madelung constant; R is the mean internuclear distance in the coordination polyhedron of the solid solution; ε_i is the ionicity of the component i; c is the fitting coefficient,‡ $c/332 = c'$ (parameter c depends on the character of the chemical bond); m is the number of atoms in the chemical formula of the compound; n is the coordination number; z_M and z_X are the oxidation states of the atoms M and X, respectively, and α is the reduced Madelung constant.

It is believed that replacement in lattice sites is possible if the electronegativity difference between the ions being replaced and replacing ions is at most 0.4 units according to Pauling. For essentially covalent compounds, incorporation into the host crystal lattice is facilitated, which is the reason for extension of the miscibility limits all other factors being the same. Quantitatively, the effect of the nature of chemical bond on the replacement is given by

$$Q = b(\Delta\varepsilon)^2, \quad (2)$$

where Q is the partial enthalpy, which includes the ionicity (covalency) of the bond in the lattice (if ΔH is represented by the additive sum of increments) and b is a constant.

If the ions to be replaced and the replacing ions are similar in size ($\Delta R/R$) = 0 the energy of mixing rapidly increases as the differences in the character of chemical bond increase (*i.e.*, with an increase in $\Delta\varepsilon$). However, the limits of isomorphism are dramatically narrowed in this case. But the main condition for isomorphous replacement (dopant ion occupies a lattice site in the matrix crystal) is the size correspondence between the impurity and host ions. According to the Goldschmidt rule, the ionic radii of the replacing ion and ion to be replaced should differ by at most $\sim$15%. For instance, in the system α-Al_2O_3:Er^{III} the large difference between the ionic radii of Al^{III} and Er^{III} is the reason for localisation of Er^{III} ions in octahedral voids rather than lattice sites[80] despite equal valences of these ions. In the course of formation of crystals of the doped matrix system, changes in the ionic radius of the impurity ion can be accompanied by changes in the local symmetry of the corresponding lattice site. An increase in the size mismatch between the central ion and the ligands in the nearest coordination polyhedron can cause the coordination number (CN) to change, namely, the ionic radii differ by about 20% as the CN value changes by two. The ionic radii also vary in a similar manner as the oxidation state of the ion also changes by two. Owing to transition of the metal ion from the high-spin to the low-spin state (so-called spin 'crossover'), which is particularly characteristic of 3d-metal ions, the ion size can also vary by about 20% at the same CN value (see the Shannon–Prewitt table of crystal radii in a monograph[81] and Fig. 7). This effect is

† For the state-of-the-art of the problem of heterovalent isomorphism and corresponding rules, see Ref. 79.

‡ The constant c is proportional to the volume and compressibility β.

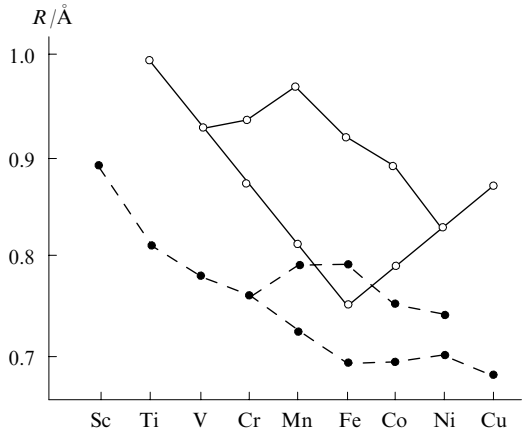


Figure 7. Crystal radii of 3d-elements plotted *vs.* element number (CN 6).[82]
The solid and dashed lines correspond to M^{2+} and M^{3+} ions, respectively. At the same charge value, the radii of the low-spin ions are less than those of the high-spin ions.

impossible for 3d-metal ions in tetrahedral oxygen environment.

The second condition for stabilisation is the entropy factor, which can cause the Gibbs energy of the system to decrease to $\Delta_r G < 0$. Compared to relatively small (often, sub-zero) enthalpies of formation of ternary or quaternary oxides from binary oxides,[83] even minor changes in the entropy can play an important role. At the same time in the case of isovalent replacement, especially at low impurity content, a significant change in the entropy of the entire system is hardly probable, especially if the nearest coordination environment of the stabilised ion remains unchanged.

It is believed[78] that the effect of the matrix crystal consists in that the crystal lattice of the compound precludes distortion of the coordination polyhedron of the impurity ion upon replacement of the matrix crystal ion. From factological point of view, this seems to be true, although the nature of this effect remains unclear. In physics of doped crystals, attempts have been reported to reveal this nature in the framework of simple physical theories like the crystal and ligand field theories.[84] In considering ions distributed over a crystalline medium, one should select, among all possible ion–crystal and ion–ion interactions, the main interactions responsible for the key properties of the system; this makes it possible to find the simplest solution. The Hamiltonian $\mathscr{H}$, which describes the interactions of the impurity ion, has the form:[85]

$$\mathscr{H} = \mathscr{H}_o + V_{ee} + V_{cr} + V_{so}. \qquad (3)$$

Here $\mathscr{H}_o$ accounts for the electron–nuclear interactions within the impurity ion; V_{ee} is the potential of the electron–electron interaction within the impurity ion; V_{cr} is the potential of the impurity ion–crystal field interaction; and V_{so} is the potential of the spin–orbit coupling.

This Hamiltonian differs from the Hamiltonian used in considering the ion in the crystal lattice (see, *e.g.*, Ref. 37) in the potential V_{cr}, which depends on the symmetry of the latice site occupied by the impurity ion in the crystal. The difference is that the symmetry of the crystal field and the corresponding description of coordination compounds are due to the properties of the central ion and the ligand; the symmetry of the impurity ion is forced by the symmetry of the local field at the site occupied by the dopant ion.

The potential V_{cr} is affected by a large number of pure lattice phenomena[37] and first of all the interaction between optical electrons of the local centre with thermal vibrations (electron–phonon interaction). This manifests itself in the electronic spectra as vibrational satellites of zero-phonon bands, which even can merge into broad absorption bands. Vibronic interaction is also the reason for migration of the absorption band intensities of activated crystals. In the case of heterovalent replacement, compensation of excess charge can involve creation of various vacancies, local-charge sites, *etc*. This manifests itself as multiple optical F-centres in corresponding electronic spectra.

The spectra of transition metal ions in crystalline matrices should exhibit various ligand field effects. The distinctive features of such spectra are as follows. The maximum of the impurity-ion absorption band does not correspond to a pure electronic transition whose energy is given by theoretical relations. This is particularly important when analysing broad bands whose widths and positions on the energy axis are only interpreted with allowance for multiphonon transitions. In this case the absorption band maximum is shifted[37] towards the short-wavelength region relative to the frequency of pure electronic transition by

$$\Delta\omega = \frac{(\delta\Omega)^2}{16\omega_f \ln 2} \qquad (4)$$

(high temperatures) and by

$$\Delta\omega = \frac{(\delta\Omega)^2}{\delta\omega_f \ln 2} \qquad (5)$$

(low temperatures). In Eqns (4) and (5) $\delta\Omega$ is the band halfwidth and ω_f is the phonon frequency.

Estimation using $\delta\Omega = 1 \times 10^3$ cm^{-1} and $\omega_f = 1 \times 10^2$ cm^{-1} gives for $\Delta\omega$ a value of the order of 10^3 cm^{-1} ($\sim 1/8$ eV) (Refs 37 and 86), which determines the pure lattice contribution to the stabilisation energy of matrix-isolated ions. The other part of this energy is due to symmetry of the ligand field and some other factors, first of all the nature of the ligand and the metal–ligand bond.

Thus, the energy effect of matrix stabilisation is, strictly speaking small. Probably, this is the reason why even attempts to qualitatively describe the phenomenon of ion stabilisation in the crystal in the framework of the ligand field theory seem not to be representative. Accumulation of errors in this approach can be due to, *e.g.*, the lack of direct relation between the ground-state population and the enthalpy contribution and to involvement of excited states in the formation of corresponding molecular orbitals. This conclusion is all the more true if we ignore the correlation effects. For instance, Hartree–Fock calculations ignoring αβ-correlation lead to a significant systematic error due to a relative overestimation of singlet-state energies. The conclusion about overestimation was drawn in *ab initio* calculations of the relative stabilities of ruthenium and osmium(VI) oxohydroxo anions in different coordination environment (relativistic density functional calculations with inclusion of spin–orbit coupling).[87]

Note that the current opinions on the nature of the matrix stabilisation effect, expressed in terms of thermodynamics, cast some doubt. They are valid for cage struc-

tures suitable for stabilisation of metal ions in low oxidation states (*e.g.*, Sc^{II} in fluorite [1]) or for disordered systems (*e.g.*, glasses [43]) rather than island structures, although it is the latter that are most often used for stabilisation of metal ions in high oxidation states. This was directly pointed in a theoretical study [88] whose authors showed that theory of isomorphous miscibility should be revised for practically important cases of crystalline matrices based on oxygen compounds of Ge^{IV}, Si^{IV}, P^{V}, As^{V}, S^{VI}, Se^{VI} and Cr^{VI}, V^{V} (in olivines, apatites and spodiosites) in the case of isomorphous replacement of Cr^{IV}, Mn^{V} and Fe^{VI} ions. In this case, the charge-transfer states change due to the d-level energies of the central ions; this leads to an efficient decrease in the parameters of Coulomb repulsion and the theory of isomorphous replacement becomes inapplicable to tetrahedral systems $\langle MO_4 \rangle$ under these conditions.§ This conclusion is of key importance when considering similar matrix systems because they are characterised by high probability of the existence of high oxidation states of heavy transition element ions (IrO_4^+, IrO_4^-, RhO_4^-).[64]

In addition, *ab initio* quantum chemical calculations of model tetrahedral clusters with Cr^{IV}, Mn^{V} and Fe^{VI} central ions and OH^- and O^{2-} ligands were carried out and the possibility of their stabilisation was analysed in terms of competition between electrostatic and covalent bonds.[88] Covalent bonds inside the tetrahedra cause the atomic charges of metal and oxygen to decrease owing to ligand-to-metal electron density transfer. Ionic bonds between tetrahedra in crystals 'act' in the opposite direction, thus favouring the formation of ionic species with most pronounced increase in the electrostatic energy. The energies of covalent bonds are additive quantities and the enthalpies of mixing are low; this allows solid solutions to exist in extended regions even if the host and guest ions (*e.g.*, Mn^{V} and P^{V} or Fe^{VI} and Cr^{VI}) are considerably different in size.

It was reported that the stability of the oxidation state of the guest metal ion in ionic matrix crystals is most probably determined by the long-range Coulomb forces with allowance for the fact that the electronic states of the stabilised ion do not change basically.[89] This fundamentally distinguishes the situation in question from the case of small guest molecules (*e.g.*, N_2, O_2, CH_4, *etc.*) in clusters that act as matrices. In that case a specific kind of rearrangement of the electronic system of guest molecules occurs (see, *e.g.*, Ref. 90) and electrostatic considerations are no longer applicable.

A key feature in the formation of a matrix system containing transition metal impurity ions is the change in the oxidation state of the guest metal ion in the course of the synthesis during transformation from the 'precursor' to the final (thermodynamically allowed) system. The oxidation state of the guest ion is 'tuned' to match that of the matrix metal ion irrespective of the type of replacement (iso- or heterovalent).

Concluding this subsection, mention may be made that thermodynamic description is only possible for macroscopic effects where the dopant concentration in the matrix system is high enough. In the case of negligible amounts of dopants, as in, *e.g.*, the system $Cs_2Fe^{VI}O_4$:Co^{VI} (Co^{VI} was detected by Mössbauer emission spectroscopy ¶), the situation is more complex.[46,47] Indeed, trial calculations [91] of the Gibbs energy of formation of a very low concentration of Co^{VI} ions in the system (matrix) with the equilibrium constant $K \approx 10^{-8}$ showed that the value

$$\Delta_f G^\circ = -RT \ln K$$

is of the order of $+50$ kJ mol^{-1}. On the one hand, this can indicate the attainment of an experimentally detectable limiting (extremal) oxidation state of cobalt ion for this type of crystals and ligands in the nearest coordination environment. On the other hand, this can point to the need for some other concepts and theories to describe the change in the oxidation state.

Thus, the change in the oxidation state of matrix-stabilised metals requires an explanation. Earlier, no emphasis was placed on this issue, because in the practically used matrix systems the role of guests is, as a rule, played by relatively stable metal ions, which are often isovalent with the host metal ions.

When analysing information concerning matrix stabilisation, one may think that the lattice of the matrix crystal 'forces' the property to the impurity ion. However, the mechanism of this phenomenon is still unclear. When considering qualitatively, this could be related to a fine balance between the ionicity and covalency in crystalline matrix systems. However, the situation is much more complicated.

2. The potentials

The interaction between impurity centres and the crystal lattice leads to modification of the potential of the impurity atom and to formation of deep energy levels in the energy spectrum of the crystal; this can be associated with the appearance of a screening potential. The deep-level energies depend on both the type of defect or impurity and the character of its interaction with the crystalline environment.[2] The assumption of screening is also confirmed in the case of, *e.g.*, fluorite-like dielectric crystals.† It should be remembered that these crystals are characterised by Coulomb interaction between the cationic and anionic sublattices,[93] the latter representing a covalently bonded cage with the cationic sublattice inside. In discussing the data of spectroscopic studies of two systems, CaF_2:U^{III} and CaF_2:U^{IV} (Ref. 17), local structural changes upon replacement of Ca^{II} ion by U^{III} and U^{IV} ions in the fluorite lattice were associated [42] with corresponding lattice compensation. Moreover, it is believed that the charge states of the impurity ions, which are not characteristic of the matrix lattice, induce a screening charge or a screening potential, which stabilises the incorporated cations. Unfortunately, at present estimation of the distribution (profile) of this potential over a three-dimensional lattice is impossible even using high-end computers.

Note that the mean lattice potential estimated using a known procedure [94] taking fluorites as an example is not representative because it does not characterise local features

§ The reason why Atanasov *et al.*[88] considered crystals with oxygen tetrahedra containing low-spin 3d-metal ions at the centre is unclear. In this case the field created by the oxygen atoms is too weak to induce electron pairing.

¶ In this case the amount of dopant is about 1 mCi, which allows the equilibrium constant to be estimated at $\sim 1 \times 10^{-8}$.

† Methods of preparation and the properties of various fluoride crystals including those with impurities are summarised in a recently published fundamental treatise.[92] Among the crystals with impurities, numerous fluorite-like phases are known.

of matrix systems. Therefore, the results of rough simulation of the fluorite lattice distortion in the vicinity of Eu^{2+} and Gd^{3+} impurity ions in MF_2 (M = Ca, Sr, Ba) compounds seem to be useful.[95] In particular, incorporation of Eu^{2+} impurity ions isovalent with the Ca^{2+} ion into CaF_2 is accompanied by a slight change in the compressibility (β) of the system, which dramatically differs from the case of the Gd^{3+} impurity ion. Low-symmetry crystal field in the vicinity of both spherical impurity centres (Eu^{2+} and Gd^{3+}) induces an electric dipole moment (D) due to both the impurity centre and, which is the most important, the displacements of the fluorine ions from their equilibrium positions. In the case of heterovalent replacement the D values are considerably larger than in the case of isovalent replacement.

When estimating the significance of iso- or heterovalent doping and local potentials in corresponding crystals, the results of corresponding band structure calculations would be used as a basis. However, this was not the aim of the known studies of the CaF_2 matrix (see ‡).[93]

Displacements of the interstitial fluorine ion from the centre of the cube built of the lattice F^- ions (Fig. 8) substantiated by the results of spectroscopic and neutron diffraction studies provide indirect information on the screening potential in the vicinity of a negatively charged vacancy (even in undoped fluorite). Probably, this potential can be related to the energy barrier to migration of vacancies and interstitial atoms in the structure.

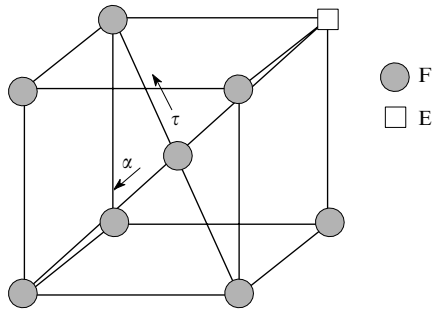


Figure 8. Displacement of interstitial fluorine atom in the anionic sublattice of fluorite.[93]
E is vacancy, α is the axial displacement and τ is the tangential displacement.

The nature and degree of compensation also remain moot questions, although it is clear that the compensation is due to the mechanism of the interaction between the components of the matrix system and defects. It is believed[96,97] that the mechanism for dielectrics involves changes in (i) position of the Fermi level, (ii) concentrations of free electrons and holes; and (iii) equilibrium concentrations of intrinsic point defects formed upon introduction of the impurity ion.

Isovalent replacement of W^{VI} by Rh^{VI} in scheelite-type crystals was studied by molecular cluster modelling, *ab initio* self-consistent field methods and using a defect-free

‡ Fluorite-like crystals (CaF_2, SrF_2, BaF_2, *etc.*) have long been studied in connection with manifestation of abnormally high ionic conductivity. More important is that they seem to be promising as optical materials in the vacuum UV region (193 nm photolithography).

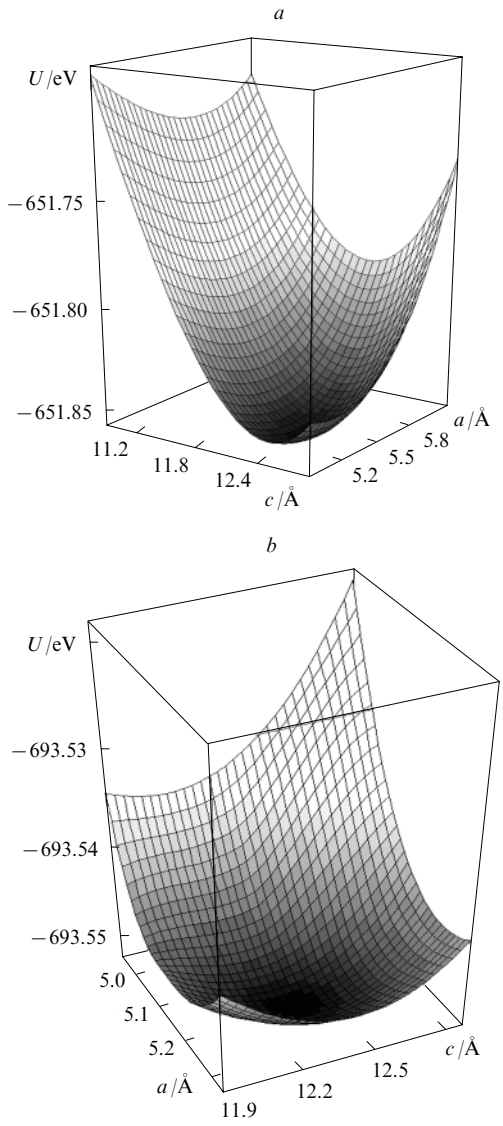


Figure 9. Cross-sections of the potential surfaces of clusters $\langle K_{10}W_5^{VI}O_{20}\rangle$ (*a*) and $\langle K_{10}W_4^{VI}Rh^{VI}O_{20}\rangle$ (*b*).[98]

model.[98] According to calculatinos, replacement of the central fragment $\langle W^{VI}O_4\rangle$ by $\langle Rh^{VI}O_4\rangle$ is energetically favourable (a well-defined, although somewhat flattened minimum on the potential surface was located) (Fig. 9). Effective charge calculations (NBO method) showed that the charges of all tungsten and oxygen atoms in the matrix remain almost unchanged upon incorporation of the $\langle Rh^{VI}O_4\rangle$ fragments. In other words, these tetrahedral fragments in the scheelite-like structure can be stabilised only through Coulomb forces.[89] Probably, the inclusion of defects (defect formation is energetically favourable) will eliminate the problem of flattening of the minimum on the potential surface.

IV. Defect formation

1. Point defects

Typical crystal lattice defects (according to Collong) in AB compounds are shown in Fig. 10. In Fig. 11 we present the electron density distribution in aluminium. A sharp charge-density maximum on the vacancy indicates a significant

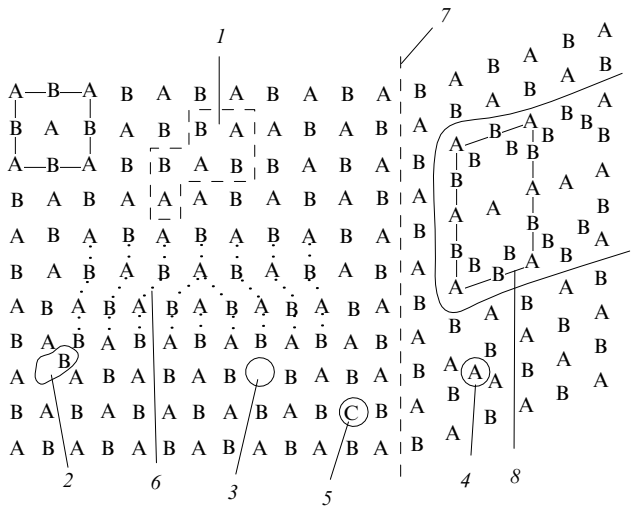


Figure 10. Different types of AB-lattice defects (according to Collong). Antistructural defects (*1*), Frenkel defects (*2*), vacancy (*3*), interstitial atom (*4*), impurity atom (*5*), edge dislocation (*6*), twin (*7*) and alien-phase inclusion (*8*).

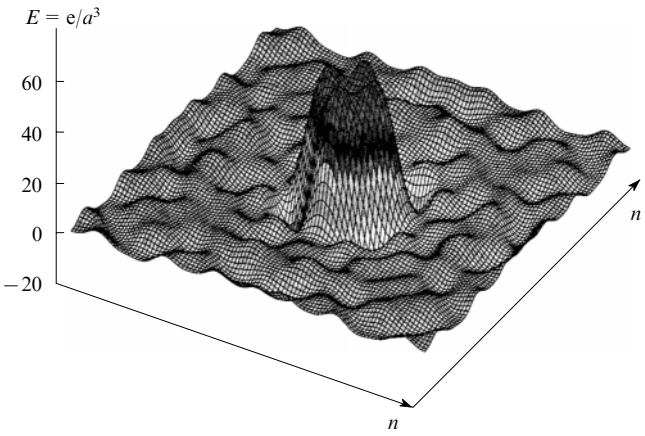


Figure 11. Visualisation of difference electron density for a vacancy in aluminium (cluster comprising 107 Al atoms).[99]
The abscissa axis: cluster size, the ordinate axis: charge density ($E = e/a^3$).

enthalpy contribution to the total energy (*i.e.*, vacancy formation is energetically favourable). This was pointed by Schottky and Wagner as long as almost eight decades ago.[100] Using methods of statistical thermodynamics, they established a relation between the defectness of the crystal lattice and the stoichiometry of inorganic compounds.

Defects have a rather strong effect on the properties of matrix systems.[101] A typical example is provided by a study[102] of the properties of aluminium yttrium garnet ($Y_3Al_5O_{12}$) crystals doped with 3d-transition metal impurity ions before and after exposure to γ-rays and high-energy electrons. Doping with the 3d-transition metal ions (concentrations $> 10^{-3}$ mass %) causes significant changes in the electronic structure and charge redistribution over defects, traps and F-centres. Two mechanisms of formation of F-centres as systems of electron (e^-) and hole (h) centres were proposed:

$$M^{n+} \longrightarrow M^{(n+1)+} + e^-$$

or

$$M^{n+} \longrightarrow M^{(n-1)+} + h.$$

The Ti, V and Cr impurities obey the first mechanism with an increase in the effective charge and the formation of an electron centre. Other 3d-transition metal ions obey the hole mechanism of formation of radiation-induced F-centres. A characteristic example is provided by chromium ions. Irradiation of crystals causes the appearance of additional optical absorption bands in the electronic spectra. The new bands are due to recharge of structural defects and to changes in the electronic state of impurity cations, namely, Cr^{IV} ions are produced as a result of the transition $Cr^{III} \rightarrow Cr^{IV}$ accompanied by trapping of an electron by the cluster $Cr^{IV}{:}[O^{2-}]_6$ and the formation of a system similar to a localised exciton $\{Cr^{IV}{:}[O^{2-}]_6 + e^-\}$. Annealing leads to thermal activation of electron and its trapping by the chromium ion

$$Cr^{IV} + e^- \longrightarrow Cr^{III}.$$

The existence of similar complexes is assumed for $KTaO_3{:}Ni^{III}$ crystals.[103] Here, two *T*-centres corresponding to different spin states of Ni^{III} ion were detected. The low-spin Ni^{III} ion ($S = 1/2$) occupies the site of the K^I ion while the high-spin Ni^{III} ion occupies the site of the Ta^V ion. The corresponding centres represent complexes built of Ni^{III} cations and oxygen anions, which are located in the nearest interstitial positions and compensate the excess charge. However, it should be noted that the possibility for the Ni^{III} ion to occupy the K^I site is unobvious, because the corresponding ionic radii differ by ~ 40%. Most probably, the Ni^{III} ion occupies appropriate interstitial positions in the $KTaO_3$ lattice.

Three types of paramagnetic centres were found in $SrF_2{:}Fe^{n+}$ (0.2 at.%) crystals.[104] Two of them were formed in the crystals after the synthesis, the third type is formed after exposure to X-rays. Two types of centres have orthorhombic symmetry. One is formed under the action of radiation on the Fe^{II} ions occupying the Sr^{II} lattice sites. This is accompanied by a $Fe^{II} \rightarrow Fe^{III}$ transition involving displacement of the product from its lattice site along the C_2 axis of the own cubic coordination polyhedron.

Heterovalent replacement of Gd^{III} ions by Sr^{II} and Ba^{II} in cobaltate $GdCoO_3$ is accompanied by the appearance of equivalent numbers of Co^{IV} ions and holes, which tend to achieve ferromagnetic ordering in the corresponding domains. As a consequence, extended ferromagnetically ordered clusters are formed around divalent ions.[105]

The *T*-centres mentioned above are very specific. For instance, for Zr^{III} ions in the $Zr^{IV}O_2{:}Y^{III}$ matrix, the optical transition corresponding to the *T*-centre§ (structureless absorption band at ~370 nm with a halfwidth of about 1 eV) represents a transition within the $4d^1$-multiplet.[106] A preferred pattern of local distortion of the *T*-centre invloves displacements of two oxygen atoms from their lattice sites towards oxygen vacancies (Fig. 12): two oxygen vacancies are displaced along the (111) direction of the crystal towards hexacoordinate Zr^{III} ion. This model provides a reasonable interpretation of the experimentally

§ This was studied by electron absorption and EPR spectroscopies.

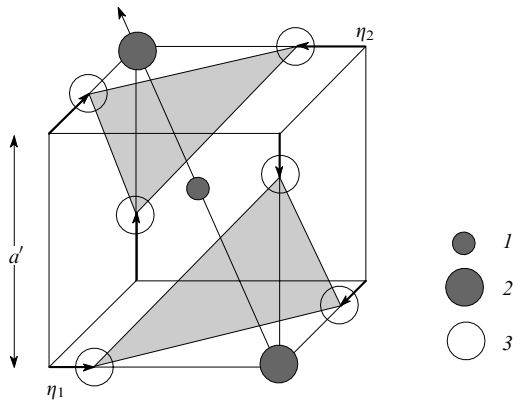


Figure 12. Structural model for a *T*-centre, which shows possible displacements (η_1 and η_2) of two oxygen atoms occupying lattice sites towards oxygen vacancies.[106]
Zr^{III} ion (*1*), oxygen vacancies (*2*) and O^{2-} ions (*3*); arrows denote deformation-induced displacements of the lattice sites.

observed of the EPR spectrum and *g*-tensor anisotropy ($g_{||} = 1.99$, $g_{\perp} = 1.85$).

Thus, impurity ions can be treated as defects, because the appearance of an alien inclusion is often accompanied by distortion of the regular system of points including that caused by interstitial location of the impurity atom. This description is of particular importance if the incorporated and matrix ions are in different charge states, because in this case a significant role is played by not only mismatch in the geometric parameters, but also vacancies, inclusion defects and various electronic defects, which ensure electroneutrality of the unit cell (see above).

Recently, the problem of defect formation has been increasingly important in connection with the need for fabrication of various items. The matrix technique appeared to be important for imparting necessary electric and magnetic properties to modern materials, *i.e.*, HTSC. For instance, small concentrations of impurities introduced into $YBa_2Cu_3O_7$ superconductor [107] are either 'dissolved' in the lattice, thus forming point defects and causing changes in the electronic structure, electrophysical and magnetic properties,[108] or isolated as constituents of nanoscale inclusions of non-superconducting phases.

A very recent study [109] in this field seems to be quite interesting. The authors [109] studied changes in the temperature dependences of the coefficients of thermal emf of the system $Tl_2Ba_2Ca_{1-x}Y_xCu_{2-y}Co_yO_z$ with the dopant (yttrium impurity) concentration. Parameters of the energy band spectrum and system of charge carriers were determined and the character and mechanism of their changes on going to the lightly doped regime, as well as the dynamics of superconducting properties were analysed.

Yet another example of the influence of doping on the properties of systems is provided by an electron microscopy study [110] dealing with the effect of iron doping on the charge ordering in manganites $La_{0.33}Ca_{0.66}Mn_{1-y}Fe_yO_3$ ($y = 0.005$). In particular, it was shown that doping with iron (5 at.%) causes a decrease in the charge ordering temperature by 50 K and the formation of a incommesurate superstructure. The superstructure unit of the doped compound includes a number of ordering defects, namely, quadruplication of the unit cell, numerous displacements along the *a* axis and dislocation defects, which are responsible for incommensurability of the structure. The decrease in the charge ordering temperature as a result of the doping with iron and incommensurability of the superstructure correlate with the change in the concentration of 'Jahn–Teller' Mn^{III} ions as a result of their replacement by 'non-Jahn–Teller' Fe^{III} ions.

2. Extended defects

The description of matrix systems based on the formation of point defects on doping is of course simplified. Probably, this approach is applicable in studies of incorporation of a few ions into the lattice, where the impurity atoms arrive at known structural sites and one can consider a corresponding charge compensation.[111] Usually, this is characteristic of metal ions in moderate oxidation states.[26,27] The situation is complicated for metals in high oxidation states, especially, for those which can form the so-called oxygenyl derivatives (VO^+, VO_2^+, RuO_3^+, UO_2^{2+}, *etc.*) or where an atomic group (complex) is incorporated into the lattice.

This can be illustrated by the results of studies [112,113] on incorporation of $[IrГ_6]^{3-}$ complexes (ligands $Г^- = Br^-$, Cl^-, CN^-) into the AgГ lattice (NaCl structural type) (Fig. 13) without structural distortion. The impurities were introduced at different stages of the growth of microcrystals, which ensured a specified location of the impurity; the

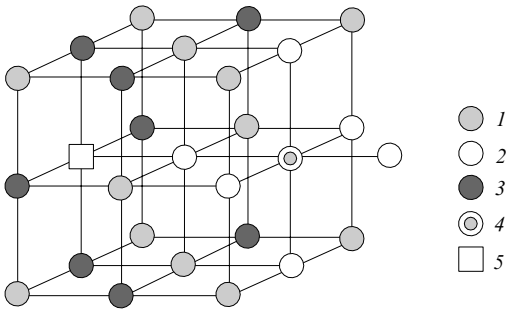


Figure 13. Embedding of a complex of hexacoordinate metal (M^{n+}) with ligands (L^-) into the AgГ (Г = Br, Cl) lattice.[113]
Ag^+ ions (*1*), L^- anions (*1*), Cl^-/Br^- ions (*3*), M^{n+} (*4*) and vacancy (*5*).

optimal impurity concentration was $(1-2) \times 10^{-8}$ moles of Ir^{III} per mole of Ag for cubic microcrystals. It was shown that incorporation of the $[IrCl_6]^{3-}$ complex into the lattice is accompanied by the appearance of local energy states in the forbidden band of AgГ. These states act as electron traps¶ of depth $\sim$0.2 eV with respect to the conduction band. Impurities violate the balance of the Frenkel defects; therefore, two vacancies $Ag_{\square}^-$ (hole traps $\sim$ 0.4 eV deep) are formed near the Ir^{III} ion to retain electroneutrality of the lattice. In explaining the behaviour of the dopant ions the authors of these studies assumed the possibility of, first, a reversible electron trapping by the iridium centre

$$[Ir^{III} \cdot 2\,Ag_{\square}^-] + e^- \rightleftharpoons [Ir^{II} \cdot 2\,Ag_{\square}^-],$$

¶ Trapping, or the so-called autolocalised, electron and hole states have long been known;[114] they represent shallow local minima on the potential surface.

(in this case the trapped electron no longer participates in fast recombination) and, second, reversible hole trapping with the formation of a vacancy centre (V)

$$[Ir^{III} \cdot 2Ag^{-}_{\square}] + p^{+} \rightleftharpoons [Ir^{III} \cdot Ag^{-}_{\square} \cdot V].$$

It was also shown that electrons temporarily trapped by the iridium centre and not participating in recombination are involved in the formation of the hidden image centre. As a result of regeneration (owing to reversibility of the first process), the iridium centre can act as an electron trap, which will lead to slowing down recombination and to changes in the kinetic parameters of photolysis of AgГ.†

Thus, this case the authors also tried to conventionally describe the situation as the formation of point defects and corresponding traps. At the same time, it is clear that the inclusion of incorporation of the complex ion into the lattice should reveal some peculiar features when the traditional approach is applied to matrix systems.

If atoms of a mainly ionic complex can be incorporated into the matrix lattice, the traditional approach can practically be implemented with ease. The situation becomes more complicated when metal ions in sufficiently high oxidation states form more or less stable covalently bonded groups. In this case, attempts to describe corresponding matrix systems can face severe problems. For instance, the authors of a study [115] of the optical spectra of the system $SrWO_4:U^{VI}$ believe that U^{VI} ions are located at the centre of a tetrahedron, which replaces $\langle WO_4 \rangle$ tetrahedron in the scheelite structure. They ignored the formation of uranyl fragments (characteristic feature of the U^{VI} ion) and explained hole burning under the action of optical excitation (activation energy ~ 0.013 eV) by uranium atomic displacements from the centre of the tetrahedron along the C_2 axis. We believe that this interpretation of hole burning is not realistic. In this case, one should consider some other type of defects rather than point defects. For instance, the properties of doped zinc sulfides and selenides are strongly affected by dislocations moving in the case of plastic deformation and bearing an electric charge of about $0.7\,e^-$ per site located in the dislocation line.[116] The existence [117] of such charges (Bürgers vectors) is responsible for the development of phenomena characteristic of a system of charged particles (*e.g.*, screening of elastic dislocation field) in corresponding dislocation ensembles.

Note that the procedure for taking account of such defects in theoretical analysis is still unclear, especially for insulators. Probably, it is these difficulties that gave the authors of Ref. 82 an impetus to consider a defect-free case, which implies the need for revision of the theory of isomorphous miscibility for crystalline oxide matrices in the case of isomorphous replacement with tetraoxo complexes containing central Cr^{IV}, Mn^{V} and Fe^{VI} ions. Assumptions of the existence of complexes $\{Cr^{IV}:[O^{2-}]_6 + e^-\}$ or $\{Ni^{III}:O^{2-}\}$ seem to be an *ad hoc* solution, which implicitly accounts for the highlighted feature.

Problems in the description of matrix systems are most often due to aggregation of defects and clustering. Thermodynamic estimates showed that the distribution of impurity atoms over various types of sites differs from random distribution even at high temperatures.[97,98] Two reasons for clustering [118] include the energy preferableness of this process and instability of uniform distribution of impurity atoms. At a rather high density defects, lattice distortions generate a defect flux, which flows against the concentration gradient; this is not necessarily accompanied by lattice disordering. This assumption is in agreement with the known trend towards retention of ordering in the crystal lattices of nonstoichiometric compounds belonging to various structural types due to formation of extended defects (crystallographic shift planes, domain walls, antiphase and twin boundaries, *etc.*),‡ including the case of small deviations from stoichiometry.[119]

In this connection, studies in the field of semiconductor physics are of interest despite their specific character, that is, the use, as a rule, of covalent or molecular crystals, which are either treated in some way (*e.g.,* irradiated) or doped. For instance, two classes of defects existing in different spatial configurations (with strong and weak electron–atom interaction) were reported [120] in studies of the electronic properties of defects in semiconductors. The first type of defects includes two carbon atoms (an interstitial atom and a lattice site atom) and donor-acceptor pairs in crystalline silicon. The second type of defects includes the interstitial boron atom in the silicon lattice.

In the framework of this review is seems interesting to consider the situation with more ionic compounds and unusual semiconductors, first of all CdF_2 (fluorite structural type) and products of its doping, for which the formation of practically valuable metastable optical centres was reported.§ This depends on the electronic structure and character of chemical bonding in crystals, which vary as a result of doping and due to changes in the oxidation state of impurity.

Valuable information on changes in the parameters of chemical bonding and oxidation state can be obtained using the cluster modelling method. For instance, this technique was used [122] to obtain a general picture of formation of metastable donor and acceptor centres in classical semiconductors and in ionic semiconductor CdF_2 (only donor centres are possible for the latter). Doping CdF_2 with gallium and indium atoms leads to considerable enhancement of the covalent component of the chemical bond in the system $CdF_2:M$ ($M = Ga^{III}$, In^{III}). This is accompanied by the appearance of donor centres due to trapping an extra electron by the defect.[123] In the fluorite-type lattice, localisation of an extra electron pair (lone pair of the impurity atom) on the same bond is impossible without local structural distortion. The appearance of the lone electron pair on the cation causes cleavage of the bonds with the ligands located on a cube face, displacement of the cation towards the nearest interstitial position and the formation of the symmetry centre C_{4v}. This was confirmed experimentally. Doping CdF_2 with Sc^{III}, Y^{III} and La^{III} ions leads to enhancement of ionic character of the chemical bond in the corresponding matrix system and excludes significant distortion of the crystal lattice, which is an inevitable companion to the formation of donor centres.

† This makes the formation of the hidden-image centre more preferable than electron–hole recombination and thus leads to an increase in photosensitivity.[113]

‡ They are often formed during nanostructuration of materials.

§ Crystals containing metastable impurity centres (so-called *DX*-centres) serve a basis for efficient holographic media (see, *e.g.*, Ref. 121). The *DX*-state is usually related to the presence of a lone electron pair in the impurity atom.

V. The non-equilibrium and matrix stabilisation

The formation of a matrix system undoubtedly involves redistribution of holes, electrons and/or various quasi-particles involved in the process in the three-dimensional crystal space, which is accompanied by the formation of defects (vacancies, Frenkel and Schottky defects, dislocations, *etc*.) in products. In the case of semiconductor and conducting crystals (first of all, quasi-one-dimensional conductors) migration of defects can be monitored by, *e.g*., exposing the crystals to high-energy radiation followed by spectroscopic detection of charge carriers.[124] At the same time even in this case the systems exposed to the action of external factors have already been completely formed (and are therefore in equilibrium) and non-equilibrium produced in some way seems to be mainly local.

For instance, unique non-equilibrium processes were considered in a review[2] taking semiconductor solid solutions of lead chalcogenides (system of centres with negative correlation energy) as examples. These processes were treated as relaxation ones, which usually occur at temperatures below 100 K, and low-temperature diffusion of non-equilibrium charge carriers from the surface into the bulk of the crystal, with spatial separation of charge carriers and freezing of the non-equilibrium state. The barriers to recombination were described using the Anderson type model, which assumes the possibility of non-equivalent transfer of charge carriers from the energy level to the band and back and the existence of charge density waves with changes in the charge state of the impurity centre, which is accompanied by rearrangement in the nearest coordination environment.

Often, the Hubbard model[125] is used. Noteworthy is the well-known phase diagram for half-filled lattice sites in the mean-field model (Fig. 14). Shaded is the transient region between the paramagnetic metal and insulator, in which the electron concentration drop at the Fermi surface disappears. Figure 14 is only an illustration of the possibility of changing the conductivity type by varying the Coulomb repulsion energy. This can be done by, *e.g*., irradiation with high-energy species, doping, *etc*. Figure 15 shows the temperature dependence of the charge carrier concentration for doped copper-oxide superconductors. This concentration is related to doping, which governs charge transfer in the plane $\langle CuO_2 \rangle$.

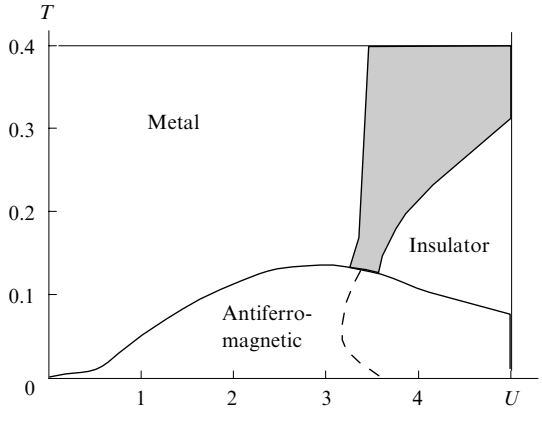


Figure 14. T,U-Phase diagram for the limiting case $d \to \infty$ and half-filled lattice sites ($n = 1$) (Hubbard model).[126]
U is the Coulomb repulsion energy, n is the number of electrons per lattice site and d is the dimension of the space.

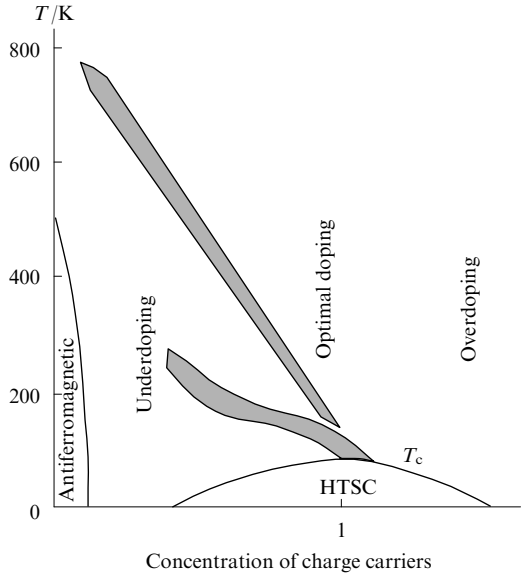


Figure 15. Diagram characterising the temperature dependence of the concentration of charge carriers for doped copper-oxide HTSC.[127]

No essential changes occur for dielectrics (insulators), which include most matrix systems containing transition metal impurity ions (especially, in high oxidation states). When irradiated or doped, they can also contain local states, in particular, the so-called *F*-centres, which have been intensively studied for long.[128]

Crystal growth techniques undoubtedly affect the form in which impurities do exist in the matrix. This can be illustrated taking the crystal growth from iron-doped SrF_2 and BaF_2 melts.[129] At low concentrations of the extra fluorine ions in the SrF_2 or BaF_2 melt, the resultant matrix system contains tetragonal iron-containing complexes $[FeF_8]^{6-}$ and $[FeF_8]^{5-}$. At high concentration of fluorine ions in the melt, $Fe^{3+}-F$ associates with fluorine ions occupying interstitial orthorhombic positions are formed in the bulk of crystals. If the iron impurity concentration in the charging material is at least 0.2 at.%, $Fe^{3+}(3d^5)-Fe^{+}(3d^7)$ dimers are stabilised in the grown BaF_2 crystals in the presence of excess fluorine ions. X-ray irradiation causes their transformation to $Fe^{1.5+}-Fe^{1.5+}$ dimers with uniformly distributed mixed valence state (for the sense of this term, see a fundamental study[130]).

If matrix systems containing impurity ions in unusually high oxidation states cannot be grown as single crystals, doping occurs during the propagation of the reaction interface. For instance, discussion of the results of doping of HTSC using self-propagating high-temperature synthesis[131] (including sonication and explosion pressing) included putting forward general considerations on possible reasons for the effects observed relating them to the superconductivity of the systems prepared. The problem of the 'reactive'

rather than local non-equilibrium was not posed owing to its clarity.

Interaction of solid reactants (one of the main methods of preparation of matrix systems) involves cleavage of chemical bonds and formation of various defects as well as formation of bonds and annealing (annihilation, recombination) of defects under a given mechanical load and a particular (although hardly detectable experimentally) temperature gradient over the sample at least at the interface. The rates of all these processes considered against the background of inhomogeneous diffusion play the key role in the synthesis of solid systems. Most often, mechanical and thermal equilibria are attained first while the true equilibrium characterised by constant chemical potential of the system is attained last. Multicomponent solid solutions are characterised by a hierarchy of atomic mobilities of various components [132] for which equilibria are attained on different time scales. If the time interval since establishment of equilibrium external conditions is shorter than the longest relaxation time, the system has no time to meet all conditions for thermodynamic equilibrium. This is the reason for difficulties in theoretical description of heterogeneous reacting systems, although attempts to overcome them have been reported. For instance, Zakharov [133] developed a phenomenological theory of quasi-equilibrium in ternary systems. In particular, he established a phase separation condition for a ternary solid solution with non-equilibrium distribution of the least mobile component and showed the existence of a temperature interval in which oppositely directed processes occur in the system. More recently, Zakharov [134] tried to describe the effect of mechanical stress in the diffusion zone on the kinetics of diffusion processes with inclusion of the volume effects and the hierarchy of component mobilities. However, the applicability of the general equations thus derived to real systems is still unclear.

Unfortunately, the problem of equilibrium in matrix systems, the more so as applied to matrix stabilisation of unstable oxidation states of transition metal ions, is usually difficult to analyse owing to the lack of necessary thermochemical data. This is due to low Gibbs free energies $\Delta_r G^\circ$ of matrix systems and to complexity (or even impossibility) of determining the $\Delta_r G^\circ$ values owing to difficulties in signal selection, large experimental errors of the available thermochemical methods and low concentrations of impurity ions in the matrix systems (data for the Gd^{III}- and Y^{III}-doped $BaCeO_3$ samples are available from Ref. 135).

Finally, it should be emphasised that matrix systems containing impurity ions in rather unstable oxidation states are usually unstable. Therefore, at present researchers only can qualitatively describe the formation of such systems, detect them and put forward hypotheses of the mechanism of matrix stabilisation.

In developing the matrix stabilisation mechanism one should first of all establish the reason for the change in the oxidation state. We believe that in crystalline matrix systems containing charged ions this is the long-range Coulomb potential, which is formed during the synthesis owing to (i) heterovalent replacement and (ii) appearance of charge-compensating defects. In the crystals containing charged impurity ions the Coulomb potential is responsible for clustering and even for the motion of clusters within the crystal (this is thermodynamically favourable [96, 97]). A typical example illustrating the aforesaid is provided by the through-the-liquid-phase effect on the distribution coefficients of small impurities in purification of semiconductor crystals,[136] which has been repeatedly confirmed in experiments.¶ The cleaning effect in melt crystallisation [139] of ionic crystals was also observed for, *e.g.*, doped fluorite-type crystals; it is associated with the motion of clusters formed during the synthesis.

The factors mentioned above can cause changes in the electronic state of impurity ions. For instance, when doping semiconductors with 3d-transition metal ions, the d-levels of these ions seem to be 'anchored' to some reference electron energy levels of the matrix (energy difference between the levels involved in intra-ion transitions equals the energy difference between the valence band tops).[140, 141] The crystal lattice can response to the recharge of impurity centres through polarisation and screening of possible charge oscillations in the impurity ions, which can, in principle, be due to heterovalent replacement.[2] A potential gradient can appear in a local domain of a crystal and create an electric field strength to 'tune' the oxidation state of impurity ions to the average oxidation state of the metal atoms in the entire lattice. For instance, electric field gradients existing near vacancies in solid solutions are high enough even at a distance of 4–5 atomic spheres from the point defect.[142] It is also believed that these gradients govern the shape of the potential energy profile along the diffusion path and the parameters of diffusion process.†

Crystallisation of a matrix system undoubtedly occurs in the presence of temperature and mass gradients; in addition, there is a particular direction of mass transfer. The mechanisms of growth of precipitate in the decomposition of solid solutions and theoretical aspects of the evolution of supersaturated solid solutions in the absence of local equilibrium have long been discussed.[145, 146]

For instance, the vacancy pump model for extended single crystals of solid solutions assumes a diffusion motion of {vacancy + impurity} complexes towards the phase precipitation boundary where the complex decomposes and the vacancy again goes to the matrix.[147] It is believed that this complex should move in a particular direction, namely, from the centre to the surface of the grain.

It cannot also be ruled out that the reaction vector in the synthesis of matrix systems containing impurity ions in unusual oxidation states by the interaction of solid reactants on heating can have another direction. We believe that these processes have much in common with the interaction in microheterogeneous systems. For instance, Fig. 16 presents a number of photographs illustrating the interac-

¶ According to Ref. 137, in the case of neutral impurities the corresponding driving force within the crystallising systems can be due to the forces of elastic interaction between impurity atoms and dislocations. This assumption was confirmed experimentally [138] taking semiconductors containing neutral impurities (In^0, Sb^0) as examples.

† It seems quite attractive to relate the hypothetical potential gradient to the electric field gradients (EFG) at the nuclei with nonzero quadrupole moments. For instance, Mössbauer experiments with a matrix system Na_2O_2:Fe^{IV} revealed an unusually high EFG at the Fe^{IV} ion,[143] which can be related to the efficiency of stabilisation of this ion. However, it is difficult to describe the whole crystal lattice from the local point of view; nevertheless, an attempt to do this was made [144] taking iron carbides as examples.

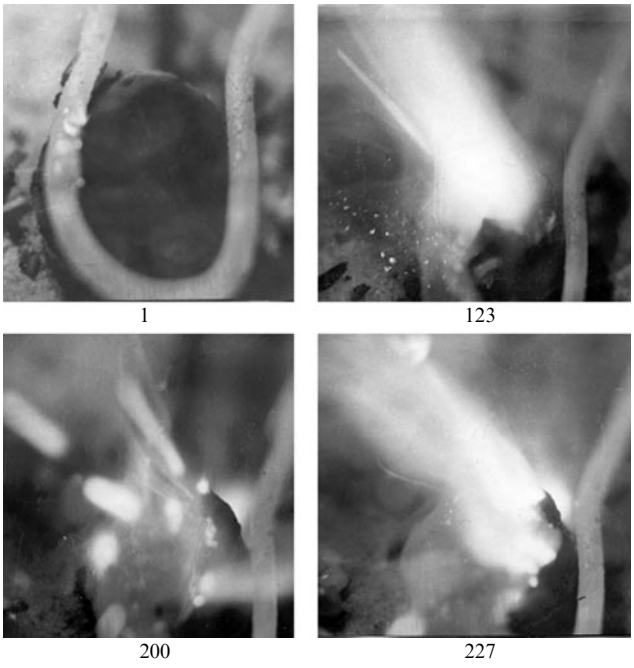


Figure 16. Combustion of a microheterogeneous system $CoF_3-Mg_3N_2$: photographs taken at different instants.
The figure below the photograph denotes its number. Parameters of experiments: camera speed 94 frames per second; time interval between two consecutive frames 0.0106 ± 0.0002 s; pelleting pressure 25 kbar, Nichrom heater coil 0.9 mm thick, heater temperature 600 °C; pellet size: height 8 mm, diameter 11 mm; pellet mass $\sim$5 g (camera man A Malyavskiy, Mosfilm, 1984).

tion of CoF_3 with Mg_3N_2. Strong exothermic interaction (with flaming) occurs in local domains of the pellet and almost does not extend to neighbouring domains; this allows the process to be treated as localised on individual particles or their aggregates. In this case one can assume that the reaction front moves into the interior of the particle as the product is removed from the particle surface. This is also indirectly confirmed by the formation of paramagnetic impurity clusters containing Mo^V in normal caesium molybdate Cs_2MoO_4 (Ref. 72). Apparently, these are the residues of molybdenum bronzes formed at moderate temperatures in the early stages of the interaction of MoO_3 with CsO_2.

The surface of small crystals of the matrix systems, which contain d-transition metal impurity ions in high and unstable oxidation states, can be involved in the matrix stabilisation mechanism. However, the surface contribution cannot be estimated at present, although it should obey the principle 'the smaller the crystals the larger the contribution'. In this connection, noteworthy is a consideration of, in particular, thermodynamic aspects of this problem.[148]

Unfortunately, a more comprehensive description of the mechanism of matrix stabilisation is currently impossible due to the lack of necessary experimental data.

Emphasise again that instability is a characteristic property of matrix systems containing impurity ions in unstable oxidation states. Therefore, in many cases single crystals necessary for physical measurements cannot be obtained, although the results of such measurements would be helpful for correct assessment of the nature of processes occurring in these systems.

VI. Identification of oxidation states in matrix systems

If multicomponent solid systems are characterised by low conductivity and contain impurity ions, the problem of proofing the existence of these ions in certain oxidation states poses. This is particularly important for unstable oxidation states. Also, establishment of the sites occupied by impurity ions is also topical; the more unstable the corresponding charge state the more significant the problem. In the latter case researchers most often deal with glassy, finely disperse and even X-ray amorphous samples, which imposes strong limitations on the methods of investigation. This mainly concerns (i) samples prepared by heating the reactants at relatively low temperatures (200–400 °C),[46–59] and (ii) nanoscale samples [*e.g.*, synthetic opals with the 'russian-doll' structure, that is, crystals are composed of spheres 300–400 Å in diameter, which in turn comprise particles of size about 100 Å (see Ref. 149)].

Mössbauer spectroscopy. ^{57}Fe (^{57}Co) Mössbauer spectroscopy is also useful for investigations of matrix systems. These nuclei occupying certain structural sites can readily change their oxidation state, which can indicate not only the presence, but also the types of defects. For instance, the quadrupole splitting and hyperfine structure parameters of the Fe^{III} ion are related to the coordination of the corresponding site and, in principle, can indicate isovalence of the ion being replaced. In studies of mixed-valence compounds,§ Mössbauer spectroscopy can be used to determine the type of the charge density wave, if the given ion can replace a 'fluctuating' component of co-operative interaction. The presence of Fe^{IV} may indicate the presence of a positively charged defect in the vicinity of structural position occupied by Fe^{III} ion (depending on a particular situation, other interpretations of the same results are also possible). In this connection, a Mössbauer study[151] of perovskite-like compounds seems to be important. The authors of that study revealed a particular cation distribution over structural positions in orthoferrites $LnFe_{2/3}Mo_{1/3}O_3$ (Ln = La, Ce, Pr, Nd). Investigations of superconducting yttrium copper-oxide systems also revealed that iron replaces copper only in the Cu(1) sites (Fig. 17), which are mainly occupied by the Fe^{IV} ions. This was confirmed by the results of Mössbauer measurements for various Fe-substituted complex oxides (Fig. 18).

Electron paramagnetic resonance. Information on the properties of matrix systems can also be obtained by EPR spectroscopy. For instance, an EPR study (data taken from Ref. 2) of the properties of well-studied lead telluride doped with mixed-valence magnetically active ions (*e.g.*, $Cr^{II/III}$) allowed one to relate the magnetic properties to the dependences of the charge carrier concentrations on the impurity content and thus to characterise the donor ability of the impurity. An EPR study[72] of normal molybdate revealed the existence of magnetic clusters containing Mo^V ions (Fig. 19). In addition, the spectral pattern suggests the existence of short-range magnetic order (magnetic correlation) similar to that found in copper oxide.

§ For instance, Goldanskii[150] considered the results of Mössbauer studies of Prussian blue (well-known mixed-valence compound) and related these data to structural features of corresponding isomers.

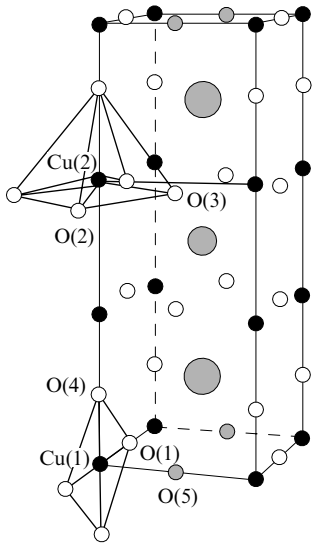


Figure 17. Characteristic structure of the crystal lattice of $YBa_2Cu_3O_{7-\delta}$-type HTSC.
Shown are two types of the environment of copper atoms. The structures of these fragments are critical to the manifestation of superconductivity (oxygen nonstoichiometry is not shown).

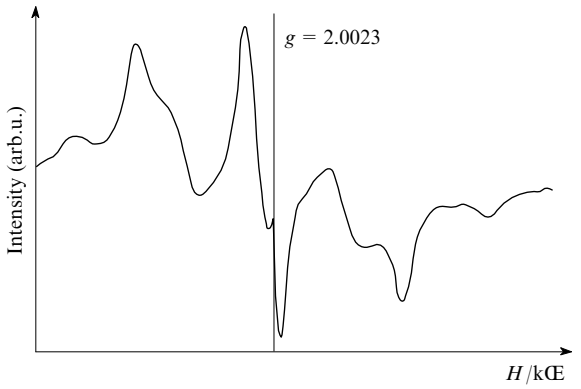


Figure 19. Typical EPR spectrum of molybdenum clusters containing Mo^{V} in a Cs_2MoO_4 sample prepared by sintering CsO_2 and MoO_3 at 350 °C and a Cs : Mo molar ratio of 2 : 1.[72]
According to Raman spectroscopy data, the major phase contains normal cesium molybdate.

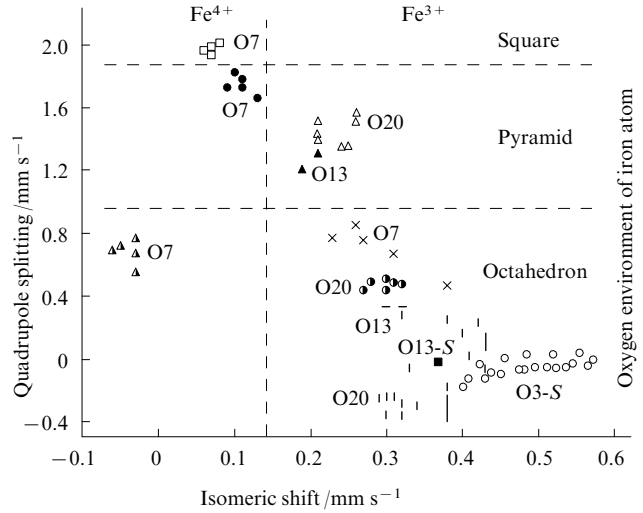


Figure 18. Mössbauer parameters of perovskites at different degree of replacement of lattice sites by iron atoms.[151]
Structural type: O7 is $YBa_2Cu_3O_{7-\delta}$, O20 is $Ln_{8-y}Sr_yCu_{8-x}Fe_xO_{20}$, O13 is $Ln_4BaCu_{5-x}Fe_xO_{13}$, O3 is orthoferrites $LnFe_{2/3}Mo_{1/3}O_3$; the symbol '*S*' denotes magnetically ordered components.

Luminescence spectroscopy is yet another probing technique suitable for studying doped metal ions. For instance, the luminescence spectra of $YBa_2Cu_3O_{7-\delta}$ can serve a reliable optical probe for diagnostics of electronic processes in these substances. In particular, it is the luminescence spectra that have shown[152] that replacement of copper atoms by Ag, Cr, Fe and Mn atoms as well as irradiation with light can be followed by electron (hole) transfer between the $\langle CuO_2\rangle$ plane and the 'charge pool' ($\langle CuO_{1-\delta}\rangle$ chain plane).

Combination of optical spectroscopy and EPR. In the cases considered above, the main condition for solving the problems posed is to choose an optimal ionic doping and the method of investigation. Using a combination of optical spectroscopy and EPR, one can also obtain information on the structure and properties of doped compounds. It is this approach that was used in a study of ferroelastics $K_3Na(CrO_4)_2$ doped with MnO_4^{2-} ions. The EPR spectrum of Mn^{VI} ion ($T \leqslant 20$ K) was identified and a broad IR luminescence band (at 8 K) with well-resolved vibronic structure (due to Jahn–Teller pseudoeffect) was found.[153] An EPR and optical spectroscopy study[154] of Cr^{III} ions incorporated into an α-Al_2O_3 matrix showed that laser excitation of the transition metal ion can be followed by the onset of frequency modulations of light in the microwave region. One can hope for the possibility of interpreting structural and antistructural defects using optical spectroscopy and EPR and appropriate probes. For instance, the Ti^{III} ion capable of forming impurity centres $\langle Ti^{III}O_6\rangle$ was proposed as a probe in the study of the structure of the nearest environment in oxides.[154] By analysing the distortion of the $\langle Ti^{III}O_6\rangle$ centres one may assess their symmetry and possible types of corresponding defects.

The interpretation[151] of Mössbauer data was facilitated by the fact that corresponding structures are known and that the samples studied were characterised by high degree of crystallinity. This allowed one to estimate the phase purity and to relate the structural data to spectroscopic data and localise particular structural positions of the impurity atoms. However, this is often impossible.

An example is provided by a study[49] of highly hygroscopic, amorphous samples of the matrix system $K_xMn_yO_z$:Fe^{V} containing a large excess of KO_2. Since the particle size in the samples corrsponded to the region of coherent X-ray scattering, in this case it is impossible to determine where the Fe^{V} impurity ion is localised, namely, in the bulk of the manganate crystals of unknown composition (on defects, dislocations, in the lattice sites, on crystallite surfaces) or even in its own oxide phase. The observed spectral characteristics only allow the quadrupole splitting (in the interval 77–298 K) and the chemical shift to be estimated. Taken altogether, these data reliably indicate the presence of Fe^{V} in the samples. One can also assume that the nearest coordination environment of Fe^{V} ions has a cubic symmetry (however, it is characteristic of both octahedral and tetrahedral environments). Thus, the localisation of Fe^{V} ions is still a moot question, like the problem of determining the composition of the matrix (if it was formed).

Location of positions occupied by paramagnetic centres in EPR studies of matrix systems is also difficult. For instance, an EPR study of normal molybdate revealed[72]

magnetic clusters containing Mo^{V} ions; however, this only allows one to assume (not state!) the effect of short-range magnetic ordering (magnetic correlation). In this case even measurements of the temperature and concentration dependences of the spectra are unsuitable, because they only substantiate the presence of clusters, leaving the problem of their localisation unsolved.

Thus, there are unsolved problems in determining the arrangement of transition metal ions in matrix crystal lattices. These problems are due to a limited potential of correspopnding physicochemical methods of investigation and to specific (and inconvenient) properties of the systems under study.

VII. Types of matrices for stabilisation of unstable oxidation states

All matrices used to stabilise unstable oxidation states can be classified into soft, rigid and intermediate ones.

Soft matrices comprise those in which the coordination bonds can 'tune' to match the size of the ion stabilised. This concerns, *e.g.*, hydroxo complexes, complexes with chelate-forming ligands and many other, where the formation of either heterobimetallic derivatives or co-existence of different-valence ions of the same metal is possible. Here, in particular, we cannot rule out the possibility of formation of polynuclear complexes with different ligands. An example is provided by a solid platinum hydroxo complex containing a superoxo platinum complex [155, 156] as impurity (detected by EPR and Raman spectroscopies) or mixed hydroxo complexes of Pt^{IV} and Fe^{IV} formed in solution (detected by Mössbauer spectroscopy).[157] A distinctive feature of these matrices is a clearly seen relation between their properties and electronic structure. This was shown by relative stability calculations using the relativistic density functional theory with inclusion of spin–orbit interaction carried out for the ruthenium and osmium oxohydroxo anions in different coordination environment as examples.[87] The results obtained are in agreement with experimental data and indicate stability of the complex $RuO_3(OH)_2^{2-}$ having CN 5, whereas $OsO_2(OH)_4^{2-}$ is stable at CN 6. The synthesis of Ru^{V} oxo complexes with L-valine, L-α-alanine and L-β-phenyl-α-alanine at pH ~ 12–13 was reported.[158, 159]

Matrices based on Na_2O_2 (and, probably, KO_2, CsO_2) also belong to soft ones. According to Mössbauer absorption spectroscopy data (T 4 K), the introduction of iron oxide into Na_2O_2 followed by heating of the mixture at 400 °C (molar ratio Na : Fe ≈ 100 : 1) resulted in samples containing Fe^{VII} and Fe^{VIII} derivatives.[54, 55] At a a Na : Fe molar ratio of ≈ 10 : 1, Fe^{IV} derivatives with unusual Mössbauer characteristics (most probably, they indicated a CN of 3, which is atypical of Fe^{IV}.[58]) were formed in the same matrix. Similar results were obtained for cobalt compounds, namely, the formation of Co^{IV} and Co^{VI} derivatives in the Na_2O_2 matrix (Mössbauer emission spectroscopy data).[59] Oxidation reactions involving Na_2O_2 and CsO_2 under rather mild conditions have been reported.[54–59] These are appropriate to attain high oxidation states of transition metals in the presence of rather strong oxidising agents (Na_2O_2 and CsO_2) and efficient stabilising agents, in particular, Cs^+ cations [160] in the reaction system.

Soft matrices undoubtedly include glasses [44] and frozen solvents, in which short-lived metal ions exist in unusual and low oxidation states.[65–70]

Rigid matrices include compounds containing dopant-accessible voids of specified size. These are zeolites, crown ethers and related compounds. For instance in zeolites the dopant size is insignificant, but the surface effects are important in some cases. In this connection we will remind earlier experiments [161] with apparent detection of Eu^{IV} in single-crystal zeolite matrix. The preparation of these samples was suggested from the shortening of the Eu–O internuclear distance to the value expected for Eu^{IV}. However, more recently it was shown by Mössbauer spectroscopy [162] that Eu^{III} and Eu^{II} rather than Eu^{IV} were stabilised and the anomaly with the distances originated from the rigid zeolite structure. Therefore, is it appropriate to consider both the effect of the matrix 'rigidity' (see above) and the sorption effects characteristic of zeolite and some other materials.[163] For instance, the influence of surface effects on stabilisation of $Cr^{6+}-V^{5+}$ and $Cr^{6+}-Ag^{+}$ ions in silica samples prepared by the sol–gel technique was studied by luminescence spectroscopy.[164] The effect of the adsorption properties of zeolite matrices on the structure and charge state of platinum carbonyl complexes was studied [165] using the local Fourier transform IR (FTIR) spectroscopy data. The possibility of formation of surface complexes with a symmetry from T_d to C_s and platinum oxidation states from +1 to +3 was shown.¶ Density functional quantum chemical modeling of surface processes was carried out. The frequency shifts and changes in the relative intensities of the signals of the dopant ions compared to those of free carbon monoxide were estimated. Note that stabilisation of ions in unusual oxidation states on the zeolite surface has been reported, although for more stable systems, *e.g.*, monovalent zinc ions (Zn_2^{2+}).[166]

V_2O_5 also belongs to rigid matrices. The introduction of Fe^{III} oxide into a V_2O_5 melt favours disproporionation of this oxidation state to Fe^{V} and Fe^{II} provided efficient quenching (in metallic mercury).[45]

The group of intermediate matrices includes compounds, which do not belong to the first two classes. This concerns, *e.g.*, an artificial (!) system KI:MnO_4^- (Ref. 167) in which a strong reducing agent and an oxidising agent co-exist. A matrix system based on LiF:$[Rh^{VI}O_2(OH)_4]^{2-}$ was synthesised and studied by EPR and diffusion reflection spectroscopies.[168] Analysis of the dependences of the signal intensity of the Rh^{VI} complex in the EPR spectra on the volume of the reducing agent suggests incorporation of the complex into the LiF lattice. In addition, the temperature and concentration dependences of the EPR linewidth of the Rh^{VI} complex indicate a random distribution of the dopant ions, $[Rh^{VI}O_2(OH)_4]^{2-}$, in the LiF lattice. The system NaF:Rh^{V} was obtained and disproporionation of the Rh^{V} complex was suggested based on the EPR and diffusion reflection spectroscopy data.[169] Pu^{VI}-containing matrix systems based on NaF and LiF ionic crystals (NaCl structural type) are also possible.[170, 171] The addition of ammonium fluoride to a 3×10^{-3} M solution of $[PuO_2(OH)_4]^{2-}$ in 3–5 M LiOH (or NaOH) solution is followed by trapping of plutonium (up to 30 mass %) by the LiF (or NaF) precipitate formed; then, Pu can be desorbed with a dilute $HClO_4$ solution.

¶ It is very interesting to study these systems in more detail, because odd oxidation states of platinum are very rare and usually detected at temperatures near 77 K. The possibility of stabilising these unusual charge states at higher temperatures using the surface effects is unclear as yet.

VIII. Methods of preparation of matrix systems containing transition metal impurity ions in unstable oxidation states

There are four main methods for preparation of matrix systems suitable for stabilisation of transition element ions in unstable oxidation states.

1. Solid-phase interaction of reactants taken in a corresponding molar ratio. In this case the heat treatment conditions are of great importance because the mechanism of atomic transfer is usually of diffusion nature (diffusion accelerates as the temperature increases). Raising the matrix formation temperature (*i.e.*, when using increasingly more severe conditions) makes the lattice stabilisation of metal ions in high (and extremal) oxidation states more difficult, because these ions usually exist under rather mild conditions.

2. Formation of matrix systems as a result of codeposition (co-crystallisation). The advantage of this technique is the possibility to form matrix systems at relatively low temperatures. For instance, the incorporation of Rh^{V}, Rh^{VI} and Pu^{VI} ions into the LiF and NaF crystal lattices (NaCl structural type) on their codeposition was reported.[168–171]

3. Formation of a matrix system due to surface trapping of the dopant from solution through chemisorption or (possibly) bricking of chemisorbed molecules by new portions of the matrix crystal during crystallisation. Here, the most probable is the complex mechanism, which also operates in the case of codeposition. For instance, it is codeposition of rhodium oxohydroxo complexes with various inorganic compounds that revealed the possibility of stabilising rhodium complexes in unstable higher oxidation states (+5, +6) on the surfaces of various sorbents including scheelite-type solid tungstates and molybdates.[163]

4. Formation of matrix systems using nuclear reactions (*e.g.*, β^-) in a matrix (host) ion. For instance, a nuclear reaction $^{191}Os(\beta)^{191}Ir$ occurred in OsO_4 crystals, resulting in a matrix system $Os^{VIII}O_4{:}Ir^{IX}O_4^+$ identified by Mössbauer emission spectroscopy.[60] Similarly, Cm^{V}, Cm^{VI} and Cf^{V} were stabilised in matrices of americium and berkelium compounds in the form of $Cm^{VI}O_2^{2+}$, $Cm^{V}O_2^+$ (Ref. 61) and $Cf^{V}O_2^+$ (Ref. 62) ions, respectively. They were obtained in β-decay of appropriate americium and berkelium isotopes. This method can be considered general because it allows not only transmutation of actinides to occur, but can also be applied to most other elements. It can be used to attain both unstable and quite stable oxidation states. In particular, the properties of the system $^{201}Tl_2O{:}^{201}HgO$ were studied by conversion spectroscopy. It was shown that ^{201}Hg nuclei formed *in situ* on soft γ-irradiation ($E \approx 1.5$ keV) of thallium oxide.[172] One can also attempt to practically implement transmutation of cesium β-isotope to corresponding daughter barium isotope. Of course, the electronic configuration of the dopant ion formed as a result of transmutation will remain unchanged, that is, the s^0 configuration is characteristic of not only the parent ion Cs^{I}, but also the daughter ion Ba^{II}. The only problem posed here is to identify the diamagnetic state attained.

The first two methods imply the existence of a driving force, which favours 'constitutional' incorporation of the stabilised ion into the matrix crystal. In high-temperature processes, the driving forces are of enthalpy and entropy nature, being the same as those favouring the formation of the matrix phase. Here, a significant role is played by specific features of the reaction interrface and diffusion. In many cases, including the formation of solid solutions, the efficiency of the exchange reaction is related to the possibility for the size of the label atoms (or electron configuration of particular atoms) to change, *i.e.*, to the mobility of corresponding electron cloud. Geometric criteria appear to be quite important because they characterise the effect of the thermodynamics of the mixed system matrix–dopant. In the last-mentioned method, the driving force is independent of the process chemistry. This is quite attractive. Unfortunately, detailed studies of the mechanisms of such processes in matrix systems have not been carried out so far.

Finally, noteworthy is particular interest in matrix systems containing stabilised transition metal ions in very high or low (so-called extremal) oxidation states. In this case, the observation of isomorphism may indicate a specific nature of the dopant–ligand bond. For instance, Ce^{IV}, Pr^{IV}, Nd^{IV}, Sm^{IV}, Tb^{IV}, Dy^{IV} and Tm^{IV} ions are stabilised in fluoride Cs_3LnF_7, whereas for $BaMO_3$-type oxide matrices (M = Ce, Th, U, Zr, Hf) the range of ions narrows to Pr^{IV}, Nd^{IV}, Tb^{IV} and Dy^{IV}. Taking account of this fact, one can conclude that stabilisation of highly charged ions in oxide systems is more difficult than compared to fluoride systems.[173] A representative example is also provided by the existence[174] of perovskite-like oxide $La_{1-x}Sr_xCuO_3$ ($0 \leqslant x \leqslant 0.25$), which contains not only Cu^{III}, but also Cu^{IV} impurity provided that a true Cu^{IV} compound (fluoro complex $Cs_2Cu^{IV}F_6$) is known. The observation of microisomorphism may additionally indicate a complex manner of attainment of higher (or lower) oxidation states in systems with a given character of the dopant–ligand bond. An example is provided by the systems $Cs_2Fe^{VI}O_4{:}Co^{VI}$ (Ref. 47) and $Os^{VIII}O_4{:}Ir^{IX}O_4^+$ (Ref. 60), in which the oxidation states of Co^{VI} and Ir^{IX} are probably the highest for these elements. In connection to search for extremal oxidation states of various elements the present consideration seems to be topical.

Summing up, note that the aforesaid to a great extent depends on the opinions concerning location of particular atoms (ions) or particular fragments in the structure of matter, which are based on indirect data obtained by physical and computational methods. Unfortunately, even the results obtained by the most informative local experimental methods (*e.g.*, EPR or Mössbauer spectroscopy) allow one to make only probabilistic conclusions, while computational (including quantum chemical) methods are still far from being perfect. Therefore, most often experimentalists use approximate information and choose algorithms of further investigations semi-intuitively.

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