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Characteristic features of the crystal chemistry of lanthanide molybdates and tungstates

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ABSTRACT. The review gives a systematic account and analyses the characteristic features of the chemical composition, crystal structures, and properties of lanthanide molybdates and tungstates. The structure forming role of molybdenum(VI), tungsten(VI), and the lanthanides(III) in oxide compounds is discussed within the framework of the bond valence force model and ideas concerning non-bonding intercationic interactions. The theoretical conclusions as regards the correspondence between the compositions, structures, and properties of the compounds are compared with experimental data.

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I. Introduction

The $Ln_2O_3-EO_3$ systems, where Ln = La–Lu and Y while E = Mo and W, are the few pseudobinary systems in which the existence of a large number of intermediate compounds has been reliably established. Many molybdates and tungstates exhibit a complex polymorphism. Many of them are distinguished by qualities of practical value. Refractory, luminescent, magnetic, piezoelectric and ferroelectric, and ferroelastic properties are frequently successfully combined in a single material.[1–3] The systematic study of phase formation in the $Ln_2O_3-EO_3$ systems, initiated in the 1960s, was initially designed for applied purposes and was characterised by a combined application of methods of physicochemical analysis and the determination of physical properties.

As a result of vigorous research, the phase relations in the above systems have been elucidated schematically in broad outline but this scheme is not final owing to the contradictory interpretation of individual details of these systems by different workers. There are objective reasons for this: the experimental difficulties in high-temperature studies, the multiplicity of phase transformations in the compounds formed, the characteristic features of the kinetics of the solid-phase reactions, and the difficulty and frequently the impossibility of isolating many phases as single crystals. For example, the $La_2O_3-WO_3$ system and the compounds formed in it have been frequently studied,[4–27] but there is nevertheless no complete certainty[25–27] about the reliability of the phase diagram (Fig. 1 [23]) constructed from the results of high-temperature (up to 2000 °C) X-ray diffraction analysis and differential thermal analysis (DTA) in view of the ultrafast quenching used ($\sim 10^5$ K s^{-1} [19]). Not only the width of the phase regions but also the very fact of the formation of certain chemical compounds and their composition have been questioned. In all probability these and similar controversial questions will soon be resolved by virtue of the progressive development of methods for structural chemical analysis,[28] a number of examples of which already exist.[29–34]

Literature data are now available for more than 40 structural types of lanthanide molybdates and tungstates, 24 of which have been elucidated (Table 1). Lanthanide molybdates and tungstates resemble structurally both complex transition metal oxides and typical salt-like compounds of the type of sulphates. Their crystal structures have the same characteristic features as classical inorganic compounds. This factor is particularly valuable because it facilitates the crystal-chemical analysis of the relationship between chemical composition, structure, and properties of the test systems.

II. The structure forming role of molybdenum(VI), tungsten(VI), and the lanthanides(III) in oxide compounds

In recent years a trend has arisen in descriptive inorganic crystal chemistry towards a shift of priorities from the topological and geometrical analysis of structures to the solution of problems involving bonding and non-bonding interatomic interactions.[78–80] This has been promoted to a considerable extent by the high accuracy of the determination of the positions of atoms achieved in the structural analysis of single crystals, the high speed of such analysis, and hence the creation of an extensive and rapidly increasing stock of experimental data. All these factors create favourable conditions for far-reaching theoretical generalisations whose development is passing through the stage involving the development of empirical models describing observed phenomena with a high degree of statistical reliability.

1. The bond valence force model

In analysing the characteristic features of the structures of crystals of inorganic compounds, which possess predominantly chemical bonds of the ionic type, the concepts of the ionic radius, the coordination polyhedron, and close packing are traditionally used.[81] The characteristic features of the structures of such compounds were first treated systematically by Pauling and were formulated[82] in the form of five principles (or rules) a list of which, frequently described

rather freely, can be found in the scientific literature.[81] Since the 1970s, investigators returned to Pauling's concept because a broader significance of Pauling's postulates became apparent than the author himself imagined initially.[82] In the 1980s, a quantum-mechanical justification of Pauling's rule was discovered. This applies to the greatest extent to the so called "second rule"—the electrostatic valence principle.[83]

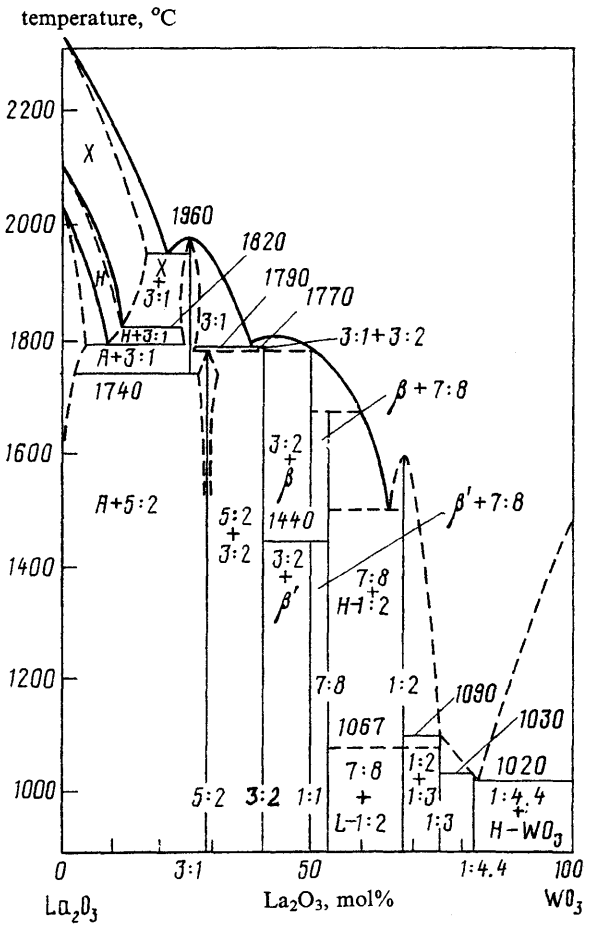


Figure 1. Phase diagram for the $La_2O_3-WO_3$ system.

In formulating this rule Pauling[82] introduced the concept of "bond strength". In the Soviet literature, the term "valentnoe usilie svyazi" ("bond valence force") became firmly established but the terms "sila", "prochnost'", "valentnost'" svyazi (bond "force", "strength", and "valence") are also used. Pauling's bond strength is defined as the ratio of the formal valence of the cation (V_M) to its coordination number (CN_M):

$$S = V_M/CN_M. \quad (1)$$

The original formulation of the rule was as follows:[82] in a stable coordination structure, the electrical charge of each anion tends to compensate for the force of the electrostatic valence bonds originating from the cations at the centres of the polyhedra whose vertices are occupied by the anion. Zachariasen[84] gives a somewhat different formulation: the sum of the valence forces of the bonds with the cations (pX), converging on the anion, neutralises the charge of the latter (V_X):

$$p\mathrm{X} = \sum_j S_j \simeq V_\mathrm{X}. \quad (2)$$

In such description, the rule has an "electrostatic" content but subsequently it began to be extended also to partially ionic covalent bonds.[85]

In the case of the simplest inorganic structures, in which there are anions of only one crystallographic kind, this rule is known to hold *a priori* by virtue of the requirement for the electrical neutrality of the crystal structure, but if the system is more complex, the exact or approximate fulfilment of this requirement cannot be regarded as self-evident. With increase in the number of elucidated structures, large groups of systems, for example heteropoly-compounds and isopoly-compounds,[86,87] were discovered, in which this rule breaks down. Thus, in the case of $[HN_3P_3(NMe_2)_6]_2Mo_6O_{19}$,[88] the six MoO_6 octahedra have a common oxygen vertex, i.e. when Eqns. (1) and (2) are formally applied one can arrive at the paradoxical conclusion that the nominally divalent oxygen atom is "neutralised" by six (pO = 6 × 6/6) valence units (v.u.) arising from the bonds with Mo(VI).

The objections against the rule became so strong that important advantages of the model such as the possibility of assigning with its aid the oxygen atoms in minerals to O^{2-}, OH^-, and H_2O were consigned to oblivion. It was not until the end of the 1960s that attention was drawn to the relation between the bond length R(M—O) and the sum of the valence forces [bond strengths] (pO) defined by Eqn. (1): the higher the value of pO, the greater the M—O bond length.[88] In the 1970s, this conclusion was supported by a multiplicity of data referring to reliably elucidated structures of oxide compounds of different classes. In 1970, Bauer[89] proposed the "extended electrostatic valence rule" based on the statistical analysis of 14 kinds of coordination polyhedra ranging from BO_3 to KO_8, according to which the following relation holds with a high degree of reliability (the correlation coefficients are close to 1.0):

$$R(\mathrm{M—O}) = a + b \cdot p\mathrm{O}, \quad (3)$$

where a and b are empirical coefficients having individual values for each kind of polyhedra. The empirical expression (3) for cations whose formal valence is less than 3 can be regarded as qualitative because in this case there is an appreciable scattering of data. Nevertheless, for cations with a higher valence, Eqn. (3) has great predictive power. Problems concerning the rapid testing of the reliability of structural determinations, the establishment of the presence of hydrogen bonds, and even the prediction of interatomic distances and bond angles in PO_4 tetrahedra on the basis of a qualitative scheme specifying the way in which these polyhedra are surrounded by other cations in concrete structures were solved.[90]

The numerical coefficients of Eqn. (3) have been analysed.[91] By means of elementary transformations, the authors[91] found that

$$(R_i - \bar{R})/\bar{R} = b(p\mathrm{O}_i - 2), \quad (4)$$

where R_i is the individual M—O_i bond length, R the average bond length in the polyhedron, and b an empirical constant. Eqn. (4) means that the change in the length of an individual bond in the polyhedron relative to the average value for the polyhedron is proportional to the difference between the valence of the oxygen

Table 1. Structural types of compounds in the $Ln_2O_3-EO_3$ systems.

Chemical composition $nLn_2O_3:mEO_3$	Formula	Structural type*	Representatives E=Mo	Representatives E=W	Crystal system space group	Representatives Ln	Representatives E	Unit cell parameters a, Å	b, Å	c, Å	angles, deg	Remarks	Refs.
3:1	Ln_6EO_{12}	Pseudofluorite	La—Er, Y	La—Lu, Y	Cubic, *F*	La	W	11.177					[9, 13, 18, 35]
	Lu_6UO_{12} *	Ho—Lu, Y	Tb—Lu, Y	$R\bar{3}$	Lu	W	9.617		9.151			[13, 36—38]
	»	La(?)Nd(?)		$R\bar{3}$ (?)	La	Mo	10.54		9.878			[37, 38]
5:2	$Ln_{10}E_2O_{21}$	$Y_{10}W_2O_{21}$ *	Nd(?)	Nd—Er, Y	*Pbcn*	Er	W	15.82	10.48	10.54			[29, 32]
	Pyrochlore	La	La	*Fm3m*	La	W	11.167					[18, 37]
«9:4»**	$Ln_{18}E_4O_{39}$	Pseudofluorite	Nd—Tm, Y		Trigonal, *R*	Nd	Mo	10.27		9.69		Subcell	[39]
«2:1»**	Ln_4EO_9	»	La, Nd		?							Not determined	[39, 40]
«7:4»**	$Ln_{14}E_4O_{33}$	»		Nd—Dy	Pseudo-*R*3	Dy	W	3.699		9.465		Subcell	[13]
		»		Ho, Y	»	Y	W	3.684		9.401		»	[13]
		»		Er—Lu	Trigonal	Er	W	7.375		9.308		»	[13]
3:2	$Ln_6E_2O_{15}$	$La_6W_2O_{15}$		La—Nd	*Cmma*	La	W	25.26	17.82	11.93			[21]
		$La_6Mo_2O_{15}$	La	La	Orthorhombic	La	Mo	12.60	5.930	8.888			[37]
1:1	Ln_2EO_6	I — Ln_2WO_6		La, Ce	Orthorhombic	La	W	7.52	12.80	10.35			[27, 41]
		II — Ln_2WO_6 *	La—Lu, Y	Ce—Ho, Y	*C*2/*c*	Nd	W	16.63	11.38	5.52	β=107.6		[42—46]
		III — Ln_2WO_6 *		Dy—Lu, Y	*P*2/*c*	Y	W	7.59	5.33	11.35	β=104.4		[45, 47, 48]
		IV — Ln_2WO_6 *		La—Ho, Y	$P\bar{4}2_1m$	Y	W	5.26		8.44			[14, 41]
		V — Ln_2WO_6 *		Pr—Er, Y	$P2_12_12_1$	Y	W	5.21	9.02	9.91			[33, 48]
		VI — Ln_2WO_6 *		Y	$P2_12_12_1$	Y	W	8.59	20.84	5.23			[49, 50]
		VII — Ln_2WO_6 *		Er—Yb	*Pbca*	Er	W	15.77	10.52	5.52			[34]
		X — Ln_2MoO_6 *	La—Sm		$I4_1/acd$	Nd	Mo	5.66		31.6			[43, 51]
		X′ — Ln_2MoO_6 *	La—Sm		$I\bar{4}cd$	La	Mo	5.80		32.0			[51]
		XI — Ln_2MoO_6	La—Nd		$Pca2_1$ (?)	Pr	Mo	5.54	16.60	5.55			[52]
«7:8»**	$Ln_{14}E_8O_{45}$	Group of polytypes		La	Hexagonal	La	W	9.05		33.25		For $n=6$	[22, 24]
«6:7»**	$Ln_{12}E_7O_{39}$	?	Nd, Pr		?							Not determined	[53]
		?		Nd	?							»	[54]
«4:5»**	$Ln_8E_5O_{27}$	?		Pr	?							»	[55]
2:3	$Ln_4E_3O_{15}$	$Nd_4W_3O_{15}$ *		La—Nd	$P4_2/nmc$	Nd	W	9.92		12.50			[11, 56]
1:2	$Ln_2E_2O_9$	I — $La_2Mo_2O_9$	La, Pr	La—Nd	Cubic	Nd	W	7.00	9.83		β=107.5*		[13, 40, 57]
		II — $Pr_2W_2O_9$ *		Ce—Gd	$P2_1/c$	Nd	W	7.64		9.22			[13, 58]
		III — $La_2W_2O_9$		La	?							Not determined	[22, 26]
1:3	$Ln_2(EO_4)_3$	A, scheelite*	La, Ce		$I4_1/a$	La	Mo	5.365		11.94			[2, 59]
		*A*1 — $La_2(MoO_4)_3$ *	La—Nd		*C*2/*c*	La	Mo	17.01	11.95	16.09	β=108.4		[2, 60]
		*A*2 — $Nd_2(MoO_4)_3$ *	Nd		*C*2	Nd	Mo	27.02	11.71	11.85	β=105.3		[59]
		*A*3 — $Eu_2(WO_4)_3$ *		La—Ho	*C*2/*c*	Eu	W	7.68	11.46	11.43	β=109.6		[61, 62]
		*A*4 — $Sm_2(MoO_4)_3$	Sm—Dy		*Cc* (?)	Eu	Mo	7.55	11.46	11.50	β=109.1		[2]
		*A*5 — $La_2(WO_4)_3$		La	?	La	W					Not determined	[14]
		L — $Gd_2(MoO_4)_3$ *	Pr—Ho		$P\bar{4}2_1m$	Gd	Mo	7.35		10.70			[2, 63—65]
		*L*1 — $Gd_2(MoO_4)_3$ *	Pr—Ho		*Pba*2	Gd	Mo	10.39	10.42	10.70			[61, 65—67]
		*L*2 — $Gd_2(MoO_4)_3$	Gd		Tetragonal	Gd	Mo	14.69		10.70			[68]
		*L*3 — $Gd_2(MoO_4)_3$	Gd		*Pna*2_1	Gd	Mo	10.39	10.42	21.40			[69]
		J — $Tb_2(MoO_4)_4$	Tb		Cubic	Tb	Mo	10.44					[61]
		G — $Dy_2(MoO_4)_3$	Dy		Cubic	Dy	Mo	6.69					[2]
		C — $Sc_2(WO_4)_3$ *	Dy—Lu, Y	Gd—Lu, Y	*Pbcn*	Lu	Mo	13.69	9.83	9.93			[2, 70, 71]
		*C*1 — $Tm_2(MoO_4)_3$	Dy—Tm		Orthorhombic	Tm	Mo	13.45	9.78	19.8	α=103,		[2]
3:10	$Ln_6E_{10}O_{39}$	$Ce_6(MoO_4)_8(Mo_2O_7)$ *	Ce		$P\bar{1}$	Ce	Mo	10.15	18.76	9.57	β=78, γ=108		[30]
1:4	$Ln_2E_4O_{15}$	$La_2Mo_4O_{15}$	La		?							Not determined	[57, 72, 73]
		$Ce_2Mo_4O_{15}$ *	Ce—Sm		$P\bar{1}$	Pr	Mo	7.39	7.51	11.82	α=89, β=97, γ=95		[31, 74]
		$Sm_2Mo_4O_{15}$	Pr—Tb		?							Not determined	[57, 73]
		$Ho_2Mo_4O_{15}$ *	Gd—Lu, Y		P2/*c*	Ho	Mo	6.82	9.59	10.53	β=105.6		[73, 75]
5:22	$Ln_{10}E_{22}O_{81}$	$Sm_{10}W_{22}O_{81}$ *		La—Sm	*Pnma*	Sm	W	35.34	21.82	3.839			[20, 76]
1:6	$Ln_2E_6O_{21}$	$Nd_2(Mo_2O_7)_3$*	La—Td		P4/*nnc*	Nd	Mo	8.97		26.45			[76, 77]

* The asterisk denotes structures which have been elucidated. ** The chemical composition has not been confirmed.

atom calculated by Eqns. (1) and (2) and its formal value, which is 2. Each type of polyhedra can then be characterised by a unique empirical parameter b. Formulae have also been proposed[90] for the estimation of the average bond lengths $\overline{R}(P-O)$ in the PO_4 tetrahedra, which take into account the number of cations surrounding the oxygen atoms and the distortion of the polyhedron.

Baur's model has narrow limits of applicability and is suitable only for relatively undistorted polyhedra. For example, it does not permit the description of the distortion in the structures of ferroelectrics belonging to the perovskite family, since according to Eqn. (4), one would have to expect the equality of all the isotypical bonds in the perovskite structure, whereas in reality, these bonds are not equivalent. It became clear from subsequent studies that the reason for this is the unsatisfactory linear approximation used for the dependence of the bond valence forces [bond strengths] on interatomic distance.

Pauling[92,93] initiated the use of the non-linear functions $S(R)$ and suggested that metallic and covalent bonds be described by the logarithmic relation

$$R = R_1 - A \ln n, \tag{5}$$

where R_1 is the length of a single bond, n the "bond number" defined as the number of delocalised electron pairs per bond, and A a coefficient (A = 0.30 Å for covalent bonds).

For ionic-covalent bonds, an expression of a similar form was used in the analysis of the interatomic geometry in V_2O_5 crystals as early as 1951.[94] Subsequently, a similar relation was used also to describe the Mo–O bonds.[95,96] The construction of plots of $S(R)$ without their analytical interpretation[97] is based on the concept of electron hybridisation. As a rule, the sums of the valence forces (bond orders) on the cations, determined by Eqn. (5), are close to the formal valences of the central atoms:

$$pM = \sum_i S_i \simeq V_M. \tag{6}$$

In the calculation of the Mo–O bond orders from the plot published by Cotton and Wing,[97] it was found that the sum of pMo appreciably exceeds the formal value of 6.

An alternative analytical expression for $S(R)$ was proposed independently by Donnay and Allmann[98] and by Pyatenko.[99] In both cases, the authors assumed that the interatomic interaction in typical inorganic structures obeys a power relation with an exponent $N > 1$ and not Coulomb's law. This approach was formulated in its final form in a study[100] where the analysis of the oxygen polyhedra in 417 reliably elucidated structures permitted the conclusion that all isotypical M–O bonds can be described by unique relations:

$$S_i = (R_i/R_1)^{-N}. \tag{7}$$

The set of empirical parameters R_1 and N was subsequently significantly extended.[101] The deviations of the values of pM calculated by Eqn. (7) from the true values of V_M are very insignificant (up to 5%). The parameters R_1 and N for the M–X bonds with X = O, F, Cl, S, P, or N, have been published.[78]

The principal qualitative feature of the model[100] consists in the fact that it does not require an "ionic" treatment of the valence balance rule and can be extended to any bonds of the ionic-covalent type. The very terms "cation" and "anion" are used not in the "electrostatic" sense but merely as designations reflecting the differences between the more electropositive partner in the chemical bond from the more electronegative one.

It has been established in recent years that the agreement with experiment achieved using the function (7) is ~30–50% worse than that obtainable with the aid of Eqn. (5), which can be written in the form[102–104]

$$S_i = \exp[(R_1 - R_i)/K], \tag{8}$$

where K and R_1 are empirical constants. The existence of a large set of experimental data, embracing 15371 polyhedra, made it possible to define the values of R_1 for the set of M–X bonds and to propose a method for the estimation of these parameters for other combinations of M and X.[103] The coefficient K was assumed to be constant for all types of bonds (K = 0.37 Å).[103] According to other data,[102,104] this parameter is specific to each set of M–X and varies in the range 0.25–0.48 Å. In view of the significant inequality of the bond lengths in the coordination polyhedron, the use of the coefficient K = 0.37 Å leads to a poorer fulfillment of the requirement for valence balance in structures than the use of values of K specific to each type of M–X bonds.[105] By virtue of the arbitrary selection of the constant of K = 0.37 Å, the empirical coefficients R_1 quoted by Brown and Altermatt[103] have values which are not entirely physically justified despite the acceptable accuracy of the results obtained by Eqn. (8).

1. In the case of polyvalent cations, the coefficients R_1 for their high oxidation states are greater than for their low oxidation states, which is itself doubtful (see also Zachariasen[84]).

2. The character of the variation of the quantities R_1 in the series of isoelectronic cations conflicts with their physical significance, since the smallest values of R_1 correspond to intermediate members of the series.

3. The previously established[100] relation between the position of the cation in the Periodic System and the values of R_1(M–O) is not manifested.

Furthermore, in the proposed method of calculation[103] no difference is drawn between transition metal cations in different spin states although the latter factor affects bond lengths.[106]

The determination of individual values of K for different types of M–X bonds involves certain difficulties, because the parameters R_1 for real structures vary in the range ±(0.015–0.020) Å relative to the statistical mean value found from the analysis of a large set of data for a wide variety of classes of compounds (simple and complex oxides, salt hydrates, complexes with involved organic ligands[105]).

The quantity R_1 depends on the characteristic features of the crystal structure.[104,105] It increases steadily with increase in the number of cations linked to the anion X participating in the M–X bond and also with decrease in their electronegativity. In the structure of hydrates, where the thermal motion of water molecules coordinated to the cation assumes significant importance, the quantity R_1 is, on the contrary, smaller than the statistical mean value. It has been suggested[105] that comparison of the values of R_1 for isotypical bonds in different structures can yield information about the effective charges of the atoms forming the bonds.

In recent years the bond valence force [bond strength] model has found a multiplicity of applications[78,98–112] by virtue of the satisfactory agreement between the results of calculations based on this simple model and experimental data. The conclusions arising from it have been confirmed by quantum-chemical methods.[83]

The model is applicable not only to the solution of traditional problems of structural analysis (including the identification of hydrogen bonds, the determination of the location of the "light" cations of the Li type,[109] the determination of the ratio of two kinds of atoms in the statistical population by the latter of one site,[100] and

the test of the validity of X-ray diffraction analysis[108]), but also to the estimation of the strengths of Lewis acids and bases[108] and the amount of ionic character of bonds.[100] Correlations have also been found between valence forces S and force constants for bond stretching[105] and the coefficients of thermal expansion of crystals.[111] Attempts have been made to use the values of S for the estimation of bond energies.[113]

Statistical studies[104,112,114] have shown that the individual values of S in the TO_4 tetrahedra, where T = Ge, P, V, S, Se, Cr, Mo, or W, obey a simple rule: they lie within the range of values from $V_T/6$ (the mean value $\bar{S}$ in the hypothetical undistorted TO_6 octahedron) and $V_T/3$ (the value of $\bar{S}$ in the hypothetical TO_3 triangle), where V_T is the formal valence of the central atom. Hence the limiting interatomic distances in these polyhedra can be found readily with the aid of Eqn. (8).

series of tetrahedra and pseudotetrahedral complexes with unshared electron pairs and the arithmetical mean values of valence forces of the bonds forming these angles. A similar relation has been found for octahedra.[104,115] Thus the method can be assessed as complementing the Gillespie method[79] for the solution of problems in coordination chemistry which has gained much popularity in recent times.

The bond valence force [bond strength] model has been used in its qualitative aspect [average valence forces determined by Eqn. (1)] for the solution of problems of the stability of crystalline substances and for the systematic treatment of data on polymorphism.[104,116]

We shall now list the principal features of the model.

1. The valence balance rule has a simple topological justification.[105] According to the principle of the superposition of the sum and of its independence of the order in which the summation is carried out, the sums ΣS with respect to all the bonds formed by any atom in the crystal structure must be equal to the formal valence of this atom. The problem thus reduces to the correctness of the determination of the function $S(R)$ and its coefficients.

2. The dependence of the individual valence forces of bonds on the length of the latter is described by an exponential law. The parameters K and R_1 in Eqn. (8) have values determined by the nature of the atoms forming the bond.

3. The "characteristic" bond valence forces (S_0) of isoelectronic cations combined with the same anion depend on the "characteristic" interatomic distances (R_0):

$$R_0 = \rho S_0^{\mu}, \qquad (9)$$

where ρ and μ are empirical constants. The term "characteristic" is applied here to the statistical mean values of R_0 and S_0. Eqn. (1) can be used to determine S_0 for a specified statistical mean coordination number CN_0. Equations of type (9) can apparently be used also for polyvalent cations.

Taking into account the information obtained using the model described above, one can formulate the following definition of the concept of the "bond valence force": bond valence forces are understood as model characteristics of interatomic interactions whose sum with respect to all the bonds formed by the given atom is numerically equal to the degree of oxidation of this atom [the number defining its oxidation state? (Ed. of Translation)].[105]

2. The structure forming role of cations

A trend has arisen in recent years to overestimate the structure-forming function of cations.[80,104,117–124] Whereas previously the analysis of crystal structures was restricted to the consideration of individual chemical bonds between atoms, i.e. to problems of coordination chemistry, nowadays the elucidation of the nature of the formation of the crystalline object as a whole has assumed decisive importance. The concept of the most compact disposition of the largest species, i.e. the largest anions and cations, has helped to some extent in elucidating the characteristics of the formation of crystal structures. However, this "packing" concept loses significance in the case of compounds with "heavy" cations.

There exist two aspects of the solution of the problem of non-bonding intercationic interactions which undoubtedly influence the dynamics of crystal lattices. Firstly, a topological approach, operating with the concept of the cationic matrix (framework, skeleton) has been developing[121] (see also Trunov et al.[104]). A method has been developed within the framework of this approach[117–124] which is based on the indentification of the planes in crystal structures most highly populated by cations. The reflections corresponding to such planes are as a rule most intense on X-ray diffraction patterns. The most compact relative disposition of cations in the planes is achieved when each cation is surrounded simultaneously by six other cations (the so-called "trigonal networks" of the 3^6 type are then formed), but there is also a possibility of "mixed" networks of the $3^3.4^2$ type with triangular and square cells, 4^4 networks with only square cells, and topologically more active networks.

It has also been suggested that individual cations can project from the planes of the networks over distances up to 0.5 Å (which amounts to 15% of the intercationic distance), while the cationic subcell sites are not subdivided as regards chemical "kind", so that vacancies can also correspond to them.[121]

According to Trunov et al.,[104] this approach can be usefully complemented by the analysis of the deformability of the cationic sublattice and the ways in which individual chemical kinds of atoms can alternate in its sites. The method for the identification of cationic motifs is used not only for the traditional classification purposes but also in considering a wide variety of solid-phase transformations, including polymorphic transformations[123] (see also Refs. 41, 46, and 48). It is also used in X-ray diffraction analysis to establish the positions of light anions if the compound includes heavy cations.[117,119]

The other approach to the analysis of the relative disposition of cations, proposed by O'Keeffe and Hyde[125,126] and by Glidewell,[127] is based on the experimentally established relatively small scatter of the "non-bond" intercationic distances when polyhedra are combined via a single common vertex regardless of the nature of the common ligand. A kind of system of "radii" has been developed, whose application ensures a satisfactory fulfillment of the additivity rule when neighbouring polyhedra are linked via a common vertex.[80] For "light" cations (including representatives of the 3*d* group of transition elements), the radii do not exceed 1.7 Å; for example, for sulphur(+6), the radius is 1.45 Å. The corresponding parameters for hexavalent molybdenum (1.90 Å) and tungsten (1.91 Å)[105] fall within the range of values 1.8–2.1 Å characteristic of the lanthanide and other "heavy" cations. When common edges are present in the polyhedra shorter (by 10–15%) intercationic contacts arise. For example, in the case of molybdenum the "intercationic interaction radius" is 1.59 Å.[105]

Thus the characteristic features of the relative disposition of cations in space are determined also by non-bonding interactions, as a result of which in the cations, with their highly developed electron core, the trend to achieve the most uniform environment comprising similar species becomes dominant, which promotes the formation of independent structural types.

We believe that the application of both schemes described above for the analysis of cationic motifs (topological and geometrical), combined with the methods of coordination chemistry (description of bonds and interbond and interligand interactions), will promote the achievement of a qualitatively new level for the consideration of the nature of the crystal structures of inorganic compounds.

3. Characteristic features of the coordination of molybdenum(VI), tungsten(VI), and the lanthanides(III) to oxgyen atoms

The crystal-chemical and stereochemical aspects of the coordination chemistry of molybdenum and tungsten compounds in the state current at the beginning of the 1970s have been described in detail.[128] During the past period, there has been a marked expansion of the number of experimental determinations and an increase in their accuracy.

A statistical survey of data on oxygen-containing molydenum(VI) and tungsten(VI) polyhedra has been carried out.[104,112] In all, information about 383 polyhedra, in which the coordination number of molybdenum varies from 4 to 7, was used. Among the total number of polyhedra, the MoO_4 tetrahedra constitute 48.6%, the MoO_5 pentagonal structures constitute 2.9%, the MoO_6 octahedra constitute 48.0%, and the MoO_7 pentagonal bipyramids constitute 0.5%. This distribution agrees with the frequency of the occurrence of particular coordinations of molydenum(VI) estimated[112] with respect to all known (including isostructural) compounds having a reliably determined coordination with respect to oxygen. The number of double molybdates alone, with heterovalent cations, taken into account in the analysis was more than 500.[104]

The tetrahedral coordination with respect to oxygen, which is so characteristic of molybdenum, is atypical for hexavalent tungsten. The WO_4 tetrahedra constitute only 10% of the total number of polyhedra, the fraction of WO_5 is 4.5%, and the fraction of WO_7 is 0.5%, so that the hexenary WO_6 coordination predominates (85%). Apart from octahedra distorted in different ways, there are also isolated examples of trigonal-prismatic coordination which occurs in similarly constructed double salts (with respect to the anion) of the type La_3WO_6X, where X = Cl_3, Br_3, or BO_3.[105]

The coefficients K and R_1 in Eqn. (8), with the aid of which the bond valence forces are determined, have the following values: K = 0.354 Å and R_1 = 1.905 Å for Mo–O; K = 0.342 Å and R_1 = 1.922 Å for W–O.[105]

The Mo–O bond lengths in the MoO_4 tetrahedra vary in the range from 1.66 to 1.91 Å, while the W–O bond lengths in the WO_4 tetrahedra vary from 1.69 to 1.92 Å. The distribution functions for the individual interatomic distances are themselves characterised by positive asymmetry[104,105] (and resemble "inverted" Morse functions) with a Gaussian "smearing" of the wings of the distributions, but the corresponding valence forces are distributed in accordance with a pseudonormal law. The most probable bond lengths in the tetrahedra are R(Mo–O) = 1.762 Å and R(W–O) = 1.775 Å (they correspond to the maxima in the distribution functions for the corresponding R_i).

The variation of the bond lengths in the tetrahedra under the influence of the "external" cationic environment are described quite satisfactorily[104] by the following expressions:

$$R(\mathrm{Mo-O}) = 1.675 + 0.186\Sigma S_{ext}, \quad (10a)$$

$$R(\mathrm{W-O}) = 1.632 + 0.272\Sigma S_{ext}, \quad (10b)$$

They take into account the contributions S_{ext}, determined from Eqn. (1), of all the "external" cations to which the given oxygen atom is coordinated. Since it is known that in the case of SO_4 tetrahedra the coefficient of ΣS_{ext} is 0.128 Å,[104] one can follow the variation of the T–O bond length in the S→Mo→W series for equal "external" influences. When the upper limit of the bond lengths in tetrahedral anions is exceeded, the coordination number of the central atom increases. This explains the low abundance of tetrahedral groups in the case of WO_4. Furthermore, it follows from Eqns. (10) presented that the formation of the "dimolybdate" groups $[Mo_2O_7]$ from two tetrahedra which are joined via one common oxygen atom, requires the formation of an Mo–O bridge bond whose length is such that it is in practice unlikely, while the formation of "ditungstate" anions appears altogether impossible. Indeed, $[Mo_2O_7]$ groups are stable only in specified instances,[129] which include, for example, the lanthanide hexamolybdates $Ln_2(Mo_2O_7)_3$,[77,112] $MgMo_2O_7$,[130] and $Ce_6(MoO_4)_8(Mo_2O_7)$,[30] which exist within narrow temperature ranges.

The length D of the O–O edges in the MoO_4 tetrahedra is from 2.66 to 3.11 Å, the statistical mean value being 2.882 Å. The distances D(O–O) are linearly related to the corresponding angles α(O–Mo–O) (correlation coefficient 0.82):

$$D(\mathrm{O-O}) = 0.25 + 0.024\alpha(\mathrm{O-Mo-O}),\ \text{Å (Ref.105).}$$

In contrast to the angles α(O–P–O) and α(O–S–O) in PO_4, SO_4, and other polyhedra, whose distortion is well described by the interbond or the non-valence interligand repulsion model,[128] the angles α(O–Mo–O) and α(O–W–O) in the MoO_4 and WO_4 tetrahedra tend to decrease as the bonds connecting these angles are shortened.[104] Under these conditions, additional oxygen atoms from the nearest tetrahedra are frequently included in the coordination sphere of Mo or W; the new atoms tend to occupy the *trans*-positions relative to the shortest Mo–O or W–O bonds in the initial polyhedron and lie over the "centres" of its expanded faces.

This feature of the distortion of the tetrahedra and the relatively high value of the parameter characterising the distance between the cations in the case of Mo and W (see the previous section) prevent the combination of the edges of the MoO_4 and WO_4 tetrahedra with other coordination polyhedra whose central atoms are high-valence ($V_M \geqslant 3$) divalent cations with an ionic radius not exceeding 1 Å. On the other hand, for sulphate ions such combination of edges is fairly typical.

With increase in the coordination number of Mo or W to 5 as a result of the approach to an O atom belonging to a neighbouring polyhedron, the dimers $[Mo_2O_8]$ or $[W_2O_8]$ are frequently formed. The length of both oxygen edges in such dimers is shortened. The pentagons usually have the form of a trigonal bipyramid in which the *trans*-influence of the axial atoms is very marked in agreement, with theory.[72,128] The bipyramids can have common oxygen edges not only with one another but also with other polyhedra.[46]

Contrary to the existing view about the similarity of the MoO_6 and WO_6 octahedra, a statistically reliably established distortion of the 2 + 2 + 2 type (gradation of the Mo–O bond lengths) is characteristic of MoO_6 octahedra.[112] Three equal-intensity maxima at R = 1.707, 1.928, 2.282 Å can be differentiated on a plot of the

R(Mo—O) distribution function. Owing to the non-linearity of the function $S(R)$ and the high degree of distortion of the polyhedra [$D_2(R)$], defined by the relation

$$D_2(R) = \left[\frac{1}{CN}\sum_{i=1}^{CN}(1 - R_i/\overline{R})^2\right]^{\frac{1}{2}}, \quad (11)$$

where $\overline{R}$ is the average bond length in the polyhedron, the arithmetical mean bond length R for the entire set of octahedra, i.e. R_m(Mo—O) = 1.973 Å, significantly exceeds the "undistorted" value R_1 = 1.905 Å. The mean distortion is $D_2(R)$ = 0.118.[112]

The WO_6 octahedra are not subject to similar "characteristic" distortions. Their average distortion is $D_2(R)$ = 0.043 and R_m = 1.940 Å for R_1 = 1.922 Å. This example is very clear, since it shows that the estimates of the size of the cations obtained using "statistical" interatomic distances may not correspond to the experimental data (including data obtained from the formula volumes of isostructural compounds) in the case of highly distorted (to different extents) polyhedra.

The "external form" of the MoO_6 and WO_6 octahedra, determined by the lengths of the oxygen edges, varies, like that of the corresponding tetrahedra,[104] to a smaller extent than all other stereochemical parameters of the polyhedra. However, whereas a unimodal distribution of the D(O—O) distances is characteristic of MoO_4, in the case of MoO_6, with the average value D_m(O—O) = 2.745 Å, a trimodal distribution is observed owing to the shortening of the lengths of oxygen edges common to other polyhedra. Three maxima can be distinguished at 2.615, 2.735, and 2.820 Å, their contributions to the overall distribution of the D(O—O) distances being 19, 35, and 46% respectively.[112] The shortest D(O—O) distances correspond to the common edges. In order to retain the average length D_m(O—O) for the octahedron, it is necessary to increase the length of the "free" edges, which is manifested by the presence of a third maximum on the distribution function curve. A similar phenomenon was also noted for GeO_6 octahedra.[114]

The average length of the edges D(O—O) in the WO_6 octahedra varies within comparatively narrow limits (2.71—2.77 Å), whereas the values of D_i specific to each individual polyhedron vary from 2.38 to 3.35 Å. The reason for this scatter is the shortening of the lengths of the common edges reflected by the appearance on the distribution function curve of a satellite maximum at 2.48 Å and a "compensating" maximum at larger distances: D(O—O) = 3.14 Å. Overall, a distortion of the external form is characteristic of the WO_6 octahedra in which there are six shortened oxygen edges and six lengthened oxygen edges in the *trans*-positions with respect to the former.

There is a strong linear correlation between the angles α(O—W—O) and the arithmetical mean values of the valence forces $\langle S$(W—O)$\rangle$ of the bonds forming this angle:

$$\alpha(\text{O—W—O}) = 51 + 39\langle S(\text{W—O})\rangle \quad (12a)$$

with a variance of ~4°. The α(O—W—O) angles range from 70° to 113°, the most acute of them being based on the common edges of the polyhedra.

A similar relation

$$\alpha(\text{O—Mo—O}) = 62 + 27\langle S(\text{Mo—O})\rangle, \quad (12b)$$

characterised by a correlation coefficient of 0.96, holds also for MoO_6.[112]

Such features of the variation of the stereochemical parameters of the octahedra make it possible to put forward two mutually consistent justifications of the small variability of the lengths of the oxygen edges D(O—O) in the absence of perturbations by additional polyhedra.

1. The increase in the angle between short bonds and the decrease in the angle between long bonds are consistent with the interbond repulsion model[79] and lead (by virtue of trigonometric relations) to similar values of D(O—O) in both cases.

2. As for the tetrahedra, the interligand non-valence interactions tend to "equalise" the lengths of the oxygen edges.

In order to account for the observed distortions of the MoO_6 and WO_6 octahedra, it is also necessary to invoke the closeness of the sums of the valence forces of the Mo—O or W—O bonds in the *trans*-positions to the value 2.0 valence units (v.u.).[104,105] This indicates the mutual dependence of the lengths of such bonds [the calculations are carried out by Eqn. (8)]. Thus in the MoO_6 octahedron the Mo atom is displaced from the centre of the polyhedron towards one of the oxygen edges, whereupon two distances R(Mo—O) are shortened compared with the "ideal" length R_1 = 1.905 Å to the "characteristic" length $R \simeq$ 1.707 Å, two R(Mo—O) distances from the molybdenum atom to the oxygen atoms on the opposite edge are lengthened to 2.282 Å, while the remaining lengths of the Mo—O bonds increase slightly to 1.928 Å. In the WO_6 octahedra, the displacements of the W atom from the centre of the polyhedron are not so marked and the cation can then be shifted not only towards two oxygen atoms forming an edge of the octahedron but also to three oxygen atoms forming one of its faces. The corresponding "short" bonds have the length R(W—O) = 1.76 Å (the W—O bond length in the "ideal" octahedron is about 1.92 Å).

This model of the distortion of the octahedra is fully consistent with the data quoted by Porai-Koshits and Atovmyan[128] and explains satisfactorily the fundamental rules governing the coupling of the MoO_6 or WO_6 octahedra formulated by the above workers[128] from the standpoint of the joint application of the concepts of the bond valence forces, the interbond repulsion and the interligand interactions.

When MoO_6 or WO_6 octahedra are combined with one another, they are grouped in such a way that the displacements of their central atoms from their geometrical centres also correspond to the intercationic repulsion model.

There are so far few experimental data on the coordination of the oxygen atoms around the lanthanide atoms and they are suitable only for a qualitative survey. A broad set of a wide variety of coordination polyhedra with coordination numbers ranging from 6 to 12 is characteristic of the lanthanides.[131] Table 2 presents the "average" coordination numbers found from statistical data for the entire set of structures known to the authors[132] in which the lanthanide atoms are coordinated only to oxygen atoms, including those incorporated in organic complex forming molecules. The "average" coordination numbers in the oxide structures proper, not containing water molecules, are also indicated in the table.[112] As a rule, the coordination number in hydrates is higher approximately by unity than in the anhydrous compounds regardless of the number of H_2O molecules. Table 2 also lists the empirical parameters in Eqn. (8) for the valence forces of the Ln—O bonds.[112]

The lower limit of the Ln—O interatomic distances is determined by the lengths of bonds having the valence force S_{max} = 0.67 v.u. [the values of R(Ln—O) can be determined from Eqn. (8)]. This valence force S_{max} corresponds to the hypothetical situation

where the oxygen atom is surrounded by only three lanthanide cations (and no other atoms). Experimental data indicate the absence of such fragments from the structures. The situation where the O atom is surrounded by Ln atoms in a tetrahedral arrangement is extremely common.[133] $S = 2/4 = 0.5$ v.u. corresponds to this situation. The coordination numbers of the lanthanide cations can then vary from 6 to 8.[105,112] For higher coordination numbers of the lanthanide atoms, such fragments are not formed.

Table 2. The average coordination numbers and parameters of Eqns. (8), (14) and (15) for the Ln–O polyhedra.[112,132]

La	n_f	CN_1	CN_2	CN_3	n_p	K, Å	R_1, Å	K^f, Å	R_1^f, Å	n'_p
La	0	8.68	8.38	8.31	94	0.354 (1)	2.175 (2)	0.310	2.220	122
Ce	1	8.65	8.41	8.20	27	0.363 (3)	2.137 (3)	0.313	2.189	46
Pr	2	8.62	8.07	8.08	43	0.270 (1)	2.214 (2)	0.316	2.172	59
Nd	3	8.48	7.85	7.97	137	0.316 (1)	2.155 (2)	0.319	2.151	172
Sm	5	8.27	7.80	7.74	45	0.339 (2)	2.101 (2)	0.326	2.114	58
Eu	6	8.21	7.40	7.63	25	0.307 (2)	2.120 (2)	0.329	2.098	46
Gd	7	8.19	7.51	7.52	70	0.298 (1)	2.114 (2)	0.332	2.083	86
Tb	8	7.83	7.19	7.40	21	0.250 (1)	2.146 (3)	0.335	2.077	23
Dy	9	7.65	7.70	7.29	26	0.304 (4)	2.080 (2)	0.338	2.046	25
Ho	10	7.40	7.25	7.18	31	0.320 (2)	2.047 (3)	0.341	2.027	48
Er	11	7.32	7.20	7.07	56	0.385 (1)	1.969 (2)	0.345	2.006	79
Tm	12	7.22	6.92	6.95	24	0.334 (6)	2.010 (3)	0.348	1.996	24
Yb	13	7.16	6.72	6.84	58	0.369 (1)	1.965 (2)	0.351	1.981	78
Lu	14	7.12	6.74	6.73	38	0.371 (2)	1.963 (3)	0.354	1.978	45

Note. Adopted notation: n_f = number of f electrons in Ln(III); CN_1 statistical mean coordination number for the set of lanthanide compounds of different classes with Ln–O bonds;[132] CN_2 = ditto for anhydrous oxide compounds;[112] CN_3 = coordination number calculated by Eqn. (13); n_p and n'_p = numbers of polyhedra for which an analysis has been carried out; K, R_1 (Å) = individual values of the parameters of the function (8); K^f, R_1^f = the same parameters calculated by Eqns. (14) and (15).[112]

The variation of the stereochemical parameters of the LnO_n oxygen polyhedra is on the whole described satisfactorily within the framework of Gillespie's method,[79] but in the structures of complex oxides with heavy cations the distortions of the polyhedra are frequently determined by the characteristic features of the intercationic geometry.[119] The abolition of the "gadolinium break" in many series of such compounds,[104] especially for a low content of the lanthanide, is remarkable.

There is a linear relation between the coordination numbers of the lanthanides in anhydrous oxide compounds and the number of f electrons n_f of the Ln^{3+} ion:

$$CN^f = 8.31(1) - 0.11(3)\,n_f \qquad (13)$$

(the correlation coefficient is -0.95). The results of the calculations of the coordination number by Eqn. (13) are presented in Table 2. The parameters K in Eqn. (8), describing the valence forces of the Ln–O bonds, are also involved in a weak linear correlation with the number of f electrons n_f:

$$K^f = 0.310 + 0.003 n_f. \qquad (14)$$

On the other hand, if one uses the values of K^f calculated by Eqn. (14) and the coefficients R_1^f are determined from the experimental interatomic distances R(Ln–O), it is found that the coefficients R_1^f are related to n_f:

$$R_1^f = 2.220\,(6) - 0.027\,(9)\,n_f^{0.85(3)} \qquad (15)$$

(the correlation coefficient is -0.9998). The values of K^f and R_1^f calculated by Eqns. (14) and (15) are also listed in Table 2. Using the equation

$$R_0 = R_1^f - K^f \ln S_0, \qquad (16)$$

it is possible to estimate with their aid the average interatomic distances R_0 and the permissible limits of the variation of the Ln–O bond lengths for any coordination numbers of the lanthanide atoms. This requires the determination by Eqn. (1) of the average bond valence force S_0 for the corresponding coordination of the lanthanide or the substitution in Eqn. (16) of the "critical" valence force S_{max} quoted above. In the calculation of the unit cell parameters of compounds by the interpolation or extrapolation methods,[105] a more reliable procedure involves the use of Ln–O bond lengths calculated by Eqn. (16) rather than the ionic radii.[106]

The set of data presented above, characterising the features of the stereochemistry of molybdenum(VI), tungsten(VI), and the lanthanides(III) in the structures of oxide compounds, makes it possible to develop a crystal-chemical approach to the explanation of the chemical compositions, structures, and properties of the crystalline phases in the $Ln_2O_3-MoO_3$ and $Ln_2O_3-WO_3$ systems.

III. Chemical compositions of the compounds formed in the $Ln_2O_3-EO_3$ systems

When molybdenum and tungsten polyhedra are condensed into finite or infinite formations (dimers, strips, layers, etc.), the chemical composition of the latter is determined by the coordination numbers of the central atoms in the initial polyhedral "seeds" and by the way in which they are combined. As regards lanthanide cations, in the presence of a high content of the lanthanide in the oxide one may expect, with a high degree of probability, the stabilisation of the cationic tetrahedra Ln_4O around the oxygen atoms not involved in the formation of the $[MoO_n]$ and $[WO_n]$ groups. The Ln_4O tetrahedra can also be combined with one another. On combining different structural units subject to the condition that the overall electroneutrality of the model crystal is maintained, one may predict the formation of the corresponding compounds.[112] From the set of hypothetical formations, it is essential to select those which are impossible or unlikely on the basis of the known stereochemical and statistical data. Certain limitations are also imposed by the functional economy rule,[104] indicating the formation of stable crystalline structures from a minimum number of fragments with fundamentally different structures.

The only possible type of group in the octahedral coordination of Mo and W atoms when the octahedra are isolated from one another is $[EO_6]$. The $[EO_5]$ fragment can be formed in several ways, the first of which involves the isolation of the EO_5 pentagons. Two other ways reduce to the sharing of elements of the octahedra: two EO_6 polyhedra are either linked in pairs via the edges or the oxygen vertices of each octahedron are shared with two neighbouring ones: $[EO_5] = EO_{4/1}O_{2/2}$. In the latter case, an additional limitation arises from the requirement that the "bridging" oxygen atoms be located in the *cis*-positions relative to one another[128] (see also

Efremov[105]). There are also several ways of organising the $[EO_4]$ fragment. Such fragments can consist of EO_4 tetrahedra isolated from one another, paired pentagons, or chains formed by the latter, i.e. $[EO_5] = EO_{3/1}O_{2/2}$, and finally systems made up of octahedra combined with one another via the four oxygen vertices of each: $[EO_4] = EO_{2/1}O_{4/2}$. In the latter case, there is a possibility of the formation of planar layers in which each polyhedron is linked to four neighbouring ones via common vertices, the formation of zig-zag chains in which the oxygen edges of the octahedra are shared, and the formation of infinite strips in which each octahedron is linked to two neighbouring ones via vertices and with one neighbouring one via a common edge.

Naturally, when the crystal structure contains more than one crystallographic species E (E = Mo, W), the composition or structural characteristics of the fragments $[EO_n]$ can be more varied. For example, the $[E_2O_7]$ fragment can be obtained not only by the sharing of the oxygen vertices of a pair of tetrahedra (which is unlikely in the case of MoO_4 and impossible in the case of WO_4) but also as a result of the combination of the EO_4 tetrahedra and EO_6 octahedra. The overall formula $[EO_4]$ can be a result of the coupling of four EO_6 octahedra to give an isolated tetramer: $[(EO_{3/1}O_{2/2}O_{1/3}.EO_{2/1}O_{2/2}O_{2/3})_2]$.[104] An increase in the complexity of the fragment reduces the probability of its existence.

We examined above the ways in which oxygen atoms are incorporated in the $[EO_n]$ fragments. In addition, oxygen atoms can be linked to the lanthanide cations only (at least four such cations) and can form the $[Ln_qO]$ fragments. The simplest of these is the tetrahedron $[Ln_4O]$. It was noted above that the E = Mo or W cations have "non-bonding intercationic interaction radii" close to those of the lanthanides. This factor promotes the formation of the structures of lanthanide molybdates and tungstates $Ln_pE_mO_n$, where $p:m \geqslant 0.67$, which are fluorite-like or are topologically similar to fluorite.

The composition of the $[Ln_qO]$ fragments is determined by the method in which the $[Ln_4O]$ tetrahedra are joined together and by the empirical crystal-chemical rules. If the numbers of tetrahedra linked to one another in each direction in space are designated by *a*, *b*, and *c*, then the general formula of the fragment assumes the form $[Ln_{(1+a+b+c+ab+bc+ca+abc)/2abc}O]$. The valence balance rule precludes the formation of a layer infinite in two directions with a thickness corresponding to two $[Ln_4O]$ tetrahedra if Ln is in the +3 oxidation state. On the other hand, the layer with $a = b = \infty$ and $c = 1$ and with the composition [LnO] can exist. An element of this layer is an infinite column having the composition $[Ln_2O]$ with the parameters $a = \infty$, $b = c = 1$. The "double" $[Ln_3O_2]$ column with $a = \infty$, $b = 2$, and $c = 1$ is also consistent with the "economy rule". More complex ways of joining together the $[Ln_4O]$ tetrahedra lead to a considerable infringement of the economy rule and can therefore be disregarded.

We shall now consider the simplest combinations in which the anionic fragments $[EO_n]$, the cationic fragments $[Ln_qO]$, and the "free" Ln species are in proportions ensuring the overall electroneutrality of the compound. The results of such studies are presented in Table 3.[112] These data can be usefully compared with those in Table 1, where the known structural types of the binary compounds in the $Ln_2O_3-EO_3$ systems are listed. The chemical formulae of the "model" compounds make it possible to describe the majority of the phases observed in the systems. The compounds in which the functional simplicity of the structural unit is combined with the "crystallographic" ratios of the stoichiometric coefficients in the chemical formulae occur most widely and exhibit the maximum structural variety and a high thermal stability. In such cases the anion-forming elements E can form, together with the Ln cations, stable cationic structural frameworks and together with their immediate oxygen environment can play, at the same time, the role of bulky units generating the structural motif. For example, the EO_6 octahedra in the Dn_2EO_6 structures are incorporated in the cationic framework (type III) and also form two-layer arrangements of networks with trigonal 3^6 (type V), square 4^4 (type IV), and mixed $3^3.4^2$ (type VI) cells.[41]

Table 3. Models of the structures of the phases in the $Ln_2O_3-EO_3$ systems.[112]

Anion	Cation		
	Ln^{3+}	$[Ln_2O]^{4+}$	$[LnO]^{+}$
$[EO_6]^{6-}$	Ln_2EO_6 1:1 4	$(Ln_2O)_3(EO_6)_2$ 3:2 +	$(LnO)_6(EO_6)$ 3:1 1
$[E_2O_{11}]^{10-}$	$Ln_{10}[E_2O_{11}]_3$ 5:6 + (?)	$(Ln_2O)_5(E_2O_{11})_2$ 5:4 —	$(LnO)_{10}(E_2O_{11})$ 5:2 1
$[EO_5]^{4-}$	$Ln_4(EO_5)_3$ 2:3 1	$(Ln_2O)(EO_5)$ 1:1 2	$(LnO)_4(EO_5)$ 2:1 +
$[E_2O_9]^{6-}$	$Ln_2E_2O_9$ 1:2 1	$(Ln_2O)_3(E_2O_9)_2$ 3:4 —	$(LnO)_6(E_2O_9)$ 3:2 +
$[EO_4]^{2-}$	$Ln_2(EO_4)_3$ 1:3 5	$(Ln_2O)(EO_4)_2$ 1:2 +	$(LnO)_2(EO_4)$ 1:1 3
$[E_2O_7]^{2-}$	$Ln_2(E_2O_7)_3$ 1:6 1	$(Ln_2O)(E_2O_7)_2$ 1:4 0	$(LnO)_2(E_2O_7)$ 1:2 0

Note. The oxide ratio $nLn_2O_3:mEO_3$ is indicated at each position in the second row. The numeral in the third row denotes the number of elucidated structural types: the + sign indicates the possibility of the formation of the given structure and the symbol 0 indicates its impossibility. A dash means that the compound has not been detected.

In another characteristic family $Ln_2(EO_4)_3$ the isolated tetrahedral anions EO_4 either play an independent structure-forming role if lanthanides at the end of the series form part of the composition of the compounds or, together with the initial members of the series, form a fluorite-like cationic framework in several varieties of the scheelite structure.[71]

The proposed modelling procedure can be extended to compounds with more complex chemical composition containing additional cations.[104,105] By analogy with the science of living nature, one can introduce the concept of the "crystal-chemical groove",[112] which indicates the possibility of the occurrence of a particular crystal structure depending on the individual features of inorganic "building units".

IV. Structure and properties

The physicochemical and certain other structure-dependent properties of compounds in the $Ln_2O_3-EO_3$ systems are examined below. The existing information about the structure of these compounds can be subdivided into four groups of facts.

1. "Neutral" lanthanide molybdates and tungstates, having the same composition $Ln_2(EO_4)_3$ as other compounds with tetrahedral anions whose central atoms E belong to Group VI of the Periodic System, are formed in all the systems.[134]

2. All the lanthanides form the compounds Ln_2EO_6. Similar lanthanide oxytellurates have been described.[135]

3. In the regions corresponding to systems with a high Ln_2O_3 content, phases with a fluorite-like structure are formed.

4. In the $Ln_2O_3-EO_3$ systems, there is a large group of compounds of different composition in the formation of which only a limited number of representatives of the lanthanide series participate.

1. The polymorphism of $Ln_2(EO_4)_3$

In terms of their physicochemical properties, the compounds $Ln_2(EO_4)_3$, can be divided into three main groups. In the so-called *C*, *L*, and *A* families, the oxygen coordination number of the lanthanide cation is 6, 7, and 8 respectively, increasing with increase in the size of the lanthanide. The properties of the molybdates and tungstates vary in parallel. An exception is the absence from $Ln_2(WO_4)_3$ of structures with a senary oxygen coordination of the lanthanide.

As a consequence of the "lanthanide" contraction, the formula volume (V/Z) of compounds having similar structures decreases smoothly in each group with increase in the atomic number of the lanthanide. The morphotropic transition to the next group is accompanied by an abrupt increase in V/Z, which is due to the different numbers and sizes of the vacancies in the frameworks of the different structures:

$$\square Ln_2^{[8]}(EO_4)_3, \quad (A)$$
$$\square_2 Ln_2^{[7]}(EO_4)_3, \quad (L)$$
$$\square_4 Ln_2^{[6]}(EO_4)_3, \quad (C)$$

The numerals in square brackets denote in this instance the coordination number of the Ln atom and the symbol □ represents a vacant site in the cationic framework.

The lattice parameters and the values of V/Z vary smoothly without the "gadolinium break". With increase in the atomic number of the lanthanide, the melting points of the compounds (with the exception of cerium compounds) increase and the temperatures of the transitions to the higher-temperature modifications fall, which agrees with the variation of the coordination number in the series of lanthanides (Table 2). In addition, the upper limit of the stability of compounds with a coordination number of 6 for lanthanides at the end of the series should increase also as a consequence of the additional stabilisation of the LnO_6 octahedra in the ideally balanced *C*-type structure at high temperatures[104] (Fig. 2). The sequence of structural rearrangements occurring on heating corresponds to the rule that the degree of balance in the structure improves, which is expressed qualitatively by the decrease in the quantities $D_2(\overline{S})$, determined by Eqn. (11) for values of pO calculated by Eqn. (2).[104]

Within the framework of one structural group of compounds $Ln_2(EO_4)_3$, the polymorphic transitions can be classified as displacements or ordering processes. The displacements entail a gain in the degree of occupation of the crystal space, for example $C \rightarrow C1$, $L \rightarrow L1$. The simplicity of the organisation of the higher-temperature "undistorted" modification and its high symmetry permit several equivalent routes to the deformation of the structure. This is a necessary condition for the manifestation by the crystals of the properties of ferroelastic materials and, following the loss of symmetry centres, also of ferroelectric materials. Statistical data show that a high symmetry of the local environment is not characteristic of the tetrahedral MoO_4 anions at the usual temperatures.[105,112]

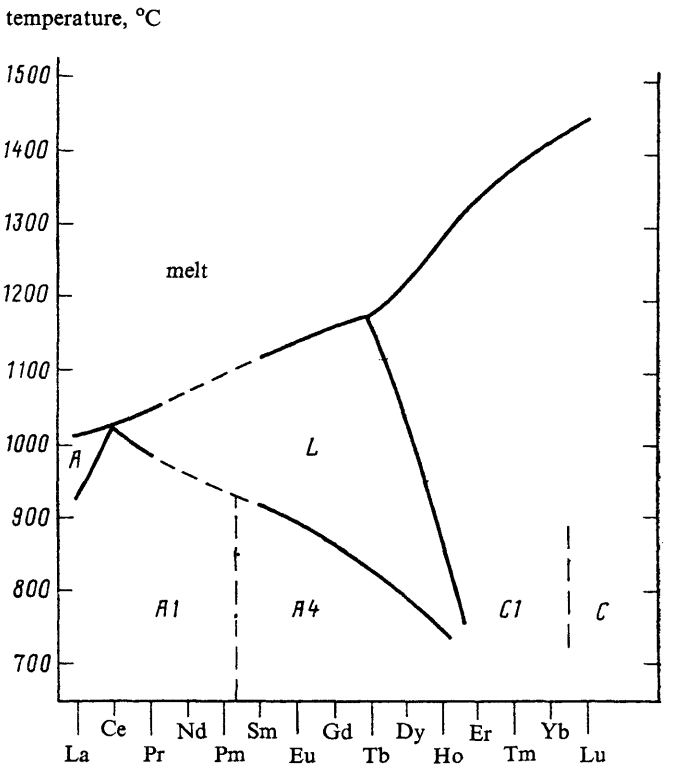


Figure 2. Temperature ranges corresponding to the existence of the polymorphic modifications of $Ln_2(MoO_4)_3$.

Another cause of such displacements of atoms relative to the initial "high temperature" structure is the endeavour by the hexavalent molybdenum and especially tungsten to increase their coordination number when the EO_4 tetrahedra are non-uniformly surrounded by highly charged cations, which is reflected in Eqns. (10). For example, the coordination number of 2/3 of the W atoms in europium tungstate (type A3) increases to 5.[62]

The next type of transformations occurring within the framework of a single structural base involves the ordering of species of different kinds, including vacancies. It proceeds via a diffusion mechanism, certain crystallographic directions proving preferable.

In practice it is frequently possible to obtain structures ordered in different ways. The scheelite-like phases (the *A* family) may serve as an example. The type of ordering can depend also on the way in which the phase is obtained, or on its previous history, and on the presence of impurity atoms in the compound.

2. Polymorphism of Ln_2EO_6

The proposed mechanism of the polymorphism is a result of systematic studies.[27,41–52] Analysis of the morphotropic transitions in this family makes it possible to discover the principal features of the variation of the structures of the most stable modifications (Fig. 3).

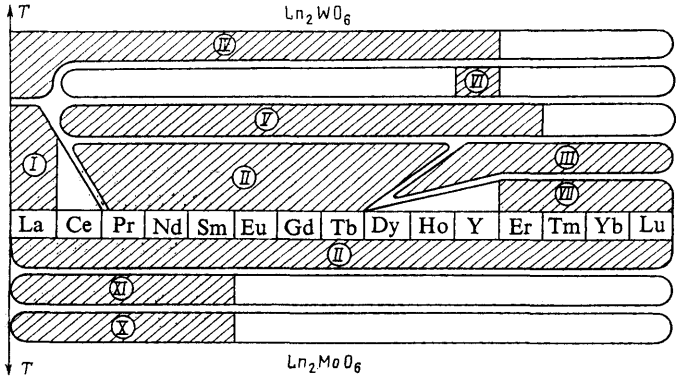


Figure 3. Schematic illustration of the polymorphism of Ln_2EO_6.

The change in the oxygen coordination number in the series of lanthanide cations is insignificant, the coordination number being in the range 8–7, decreasing from La to Lu. In structures of the intermediate members of the series, both coordination numbers occur. The coordination number of the anion-forming element (E = Mo, W) in this series show a tendency to increase from 4 (type X), through 5 (type II), to 6 (types III–VII). Lower coordination numbers are more characteristic of molybdenum in oxymolybdates than of tungsten in oxytungstates. On passing from oxymolybdates to oxytungstates in the La–Lu series, it is possible to identify changes in the structures of the compounds in which the degree of the mutual binding of the cationic tetrahedra $[Ln_4O]$—the residual units of the parent fluorite structure—is reduced. This concerns the following transitions: two-dimensionally infinite [LnO] layer in X→double $[Ln_3O_2]$ strip in II→infinite $[Ln_2O]$ column in VII→Ln^{3+} cation not involved in the formation of the $[Ln_qO]$ fragment in III–VI.

Fluorite-like cationic frameworks are characteristic of the structures of the majority of the low-temperature modifications, while the structures of the known high-temperature forms IV–VI are determined by the arrangement of large octahedral WO_6 anions which are isolated from one another.

The phase transitions between different modifications of Ln_2EO_6 are reconstructive. The reversible and readily occurring structural transformations V⇄VI⇄IV reduce to successive displacements of part of the WO_6 oxy-anions within the framework of the layer and to slight displacements of the lanthanide cations.[41] It is remarkable that all three high-temperature forms of oxytungstates are identical, whereas the low-temperature polymorphic modifications have a centrosymmetrical structure. The interconversions of the low-temperature modifications proceed via more complex pathways but they are also imagined to be subdivided into a sequence of "elementary" movements of the lanthanide cations and the elements E in steps not exceeding the typical intercationic distance of 4 Å.[46,48]

In each group of isostructural compounds, an increasing number of signs foreshadowing a change in the structural type, involving an increase in strain in contacts of the type O...O or M...M′ (M = cation), are observed as the extreme members of the series are approached. The significant shortening of one of the Ln...W edge contacts in the WO_6 and LnO_7 polyhedra on passing to the lanthanides at the end of the series is in fact responsible for the widening of the temperature range corresponding to the existence of form III with a coordination number of 8 instead of the widening of the region corresponding to the stability of structures of type V where there are seven nearest oxygen atoms in the environment of each Ln cation of both kinds.

An important structural characteristic of the majority of polymorphic modifications of Ln_2EO_6 is the presence in the latter of at least two crystallographic kinds of lanthanide atoms which in a number of instances are involved in different types of oxygen coordination. This makes it possible to "regulate" the extent of the temperature ranges corresponding to the stability of the phases on transition from the double oxides proper to the solid solutions based on them.[27]

3. Fluorite-like compounds in the Ln_2O_3–EO_3 systems

The most contradictory interpretation of the phase relations in the Ln_2O_3–EO_3 systems is in the region of a high content of the lanthanide components (in excess of 60 mol%). Compounds of several types are formed whose common feature is the involvement of fluorite (CaF_2) as the structural prototype. Whereas an octonary oxygen coordination is characteristic of the lanthanides (especially those at the beginning of the series) in the oxygen compounds (Table 2), the occurrence of coordination numbers ranging from 4 to 6 for Mo and W requires a definite rearrangement of the initial fluorite structure in order to ensure an environment characteristic of these elements. This can entail the displacements of the anions from the positions at the centres of the cationic tetrahedra to the triangular faces of the latter, the formation of anionic vacancies, and local displacements of the atoms in the non-ordered phases.

In examining the correspondence between the chemical composition of the phase and its crystal-chemical nature, one can imagine several situations.

1. Atoms of each kind wholly populate particular regular systems of points in the structures of the compounds. With the exception of the special cases of "subtraction phases" or "interstitial phases" where the ordering is complete, compounds are formed with a distinct stoichiometry and fairly narrow regions of homogeneity.

2. Anionic disordering takes place when the number of sites for the accommodation of anions, determined by the multiplicity of the regular system of points in the space group of the crystal, exceeds the actual number of anions corresponding to the chemical formula of the compound. Owing to the absence of some of the anions from the structure as a consequence of thermal motion, there is a

possibility of the migration of the remaining anions between crystallographic positions belonging to the same regular system of points. This mechanism is most probable at high temperatures. When the anions and vacancies are distributed statistically among the same positions, situations where cations of different kinds (Ln and E) are involved in oxygen coordination characteristic of them are entirely realistic.

3. Finally, at very high temperatures (in excess of 1400 °C), the crystal-chemical individuality of the cations is abolished owing to the thermal motion of the atoms, as a result of which they become statistically distributed among the sites of the initial prototype structure. The usual crystal-chemical rules which hold at the normal temperatures, apparently lose their significance under these conditions (Fig. 1).

Among the large number of "fluorite-like" phases listed in Table 1, only the structures of Ln_6EO_{12} (rhombohedral form) and $Ln_{10}E_2O_{21}$ have been reliably characterised. Furthermore, studies at high temperatures have shown that the compounds Ln_6EO_{12} give rise to broad regions of homogeneity based on the cubic fluorite structure in the vicinity of the melting points. The formation of such phases at low temperatures (1000–1200 °C) in the initial stages of the synthesis can apparently be attributed to the characteristic features of the solid-phase reactions in systems the composition of the components of which include cations with similar "radii of intercationic interactions through bonds". Such labile phases can be assessed as a kind of intermediate "activated complexes". For example, the cubic oxytungstate La_6WO_{12} in the $La_2O_3-WO_3$ system is thermodynamically stable only above 1900 °C (Fig. 1), but the synthesis from the oxides at temperatures below 1400 °C affords, as a result of the annealing of the reaction mixture for 5–20 h, a single-phase product characterised by a similar X-ray diffraction pattern.

Compounds having the approximate composition $7Ln_2O_3.4EO_3$ are in reality mixtures of phases ordered in different ways and having similar stoichiometries and fairly complex superstructures[29] like the phases in the $Ce_2O_3-CeO_2$ system.[136]

4. Compounds having other compositions

The stereochemical differences between the molybdenum and tungsten atoms coordinated to oxygen atoms begin to have an appreciable effect in the structures of lanthanide polymolybdates and polytungstates, i.e. compounds having the composition $Ln_2O_3.nEO_3$, where $n > 3$. The chemical compositions of polytungstates and polymolybdates are different. The only type of polytungstates ($Ln_{10}W_{22}O_{81}$) has a "bronzoid" structure, which consists of a complex interlinked set of WO_n pentagons, hexagons, and heptagons, each of which is joined to two similar formations via common axial oxygen vertices. This structure shows a definite similarity to that of polytantalates.[76]

Polymolybdates unexpectedly have structures which incorporate dimerised tetrahedra. The $[Mo_2O_7]$ groups can be very remote from other Mo–O anions. The temperature ranges corresponding to the stability of the compounds $Ln_2(Mo_2O_7)_3$, formed under equilibrium conditions at temperatures of the order of 650–720 °C, are extremely narrow (of the order of 30–70 °C).[77] An interesting feature of these systems is the ease of hydration of the quenched specimens (they are quenched to prevent their decomposition on cooling). Such ease is caused by the presence in their structure of large cavities combined into a single system of channels.[76] The trapped water molecules increase the coordination number of the lanthanide atoms from 8 to 9, which stabilises the structure of the monohydrate. The large hydrated crystals can be stored without change for at least 15 years.[76] On heating, the coordinated water is removed at about 280 °C, after which the compound decomposes at about 450 °C into the tetramolybdate and MoO_3; on further increase in temperature, it is reformed but this time in the region of its thermodynamic stability.[112]

In the structures of heavy lanthanide tetramolybdates $Ln_2Mo_4O_{15}$, the dimolybdate ions no longer play an independent role. They are built up to pentagonal formations by combining with neighbouring MoO_4 tetrahedra, which ultimately leads to the appearance of the $[Mo_4O_{15}]$ fragment.[75] The tetramolybdates of the lanthanides in the middle of the series contain isolated MoO_4 tetrahedra and complex polymeric fragments $[Mo_8O_{29}]$ made up of MoO_n tetrahedra, pentagons, and octahedra.[76] The formation of tetramolybdates in the structures of which there are isolated MoO_4 groups and polymer chains having the composition $[Mo_2O_7]$, made up of tetrahedra and octahedra, is characteristic of the lanthanides at the beginning of the series.[74]

On the other hand, tungstates are more widely represented when the ratios of the initial oxides are $Ln_2O_3:EO_3 > 1:3$. They contain WO_6 octahedral groups. This fact agrees well with the views described above concerning the greater tendency of tungsten(VI) compared with molybdenum(VI) to form compounds with high degrees of coordination under the influence of the "external" cationic environment. The great variety of ways in which the WO_6 octahedra can be distorted and of the types of their bonding also promotes the formation of different phases in the systems (Fig. 1).

The changes in the temperature ranges corresponding to the stability of such structures are also correlated with the degree of distortion of their constituent coordination polyhedra.

V. Conclusion

Despite the great variety of types of crystal structures of lanthanide molybdates and tungstates and the wide range of variation of the coordination numbers of E (from 4 to 7) and Ln (from 6 to 11), there is a profound relationship between the coordination numbers of the cations and their relative contents in specific structures.[112] Fig. 4 presents the changes in the "average" bond valence forces $\overline{S}_M$ in the structures of compounds of the lanthanides at the beginning, in the middle, and at the end of the series. The weighted mean value of the individual S, found by Eqn. (1), was used as $\overline{S}_M$:

$$\overline{S}_M = \left[\sum_i (n_i V_{M_i})/CN_i\right] / \sum_i n_i,$$

where V_{M_i}, CN_i, and n_i are respectively the formal valence, the coordination number, and the multiplicity of the position in the structure of each of the crystallographically different kinds of cations regardless of their chemical nature. The "generalised oxygen index" α, defined as the ratio of the number of oxygen atoms in the chemical formula of the oxide to the total number of cations, has been plotted along the abscissa axis in Fig. 4. For $Ln_pE_mO_n$, index α is equal to the ratio $n/(p+m)$; in particular, $\alpha = 2.0$ for Ln_2EO_6. The use of the index α makes it possible to compare the properties of compounds having different compositions formed in a single physicochemical system.[112]

The character of the variation of $\overline{S}_M$ with α, similar to that illustrated in Fig. 4, has been observed[112] for a wide variety of pseudobinary systems with several intermediate compounds having

known crystal structures, including compounds of the type $M_2EO_4-Ln_2(EO_4)_3$, where M is an alkali metal ranging from Li to Cs. When the compound forms several polymorphic modifications, the deviations of $\overline{S}_M$ for the high-temperature forms from the straight line joining the values of $\overline{S}_M$ for the initial components diminish.

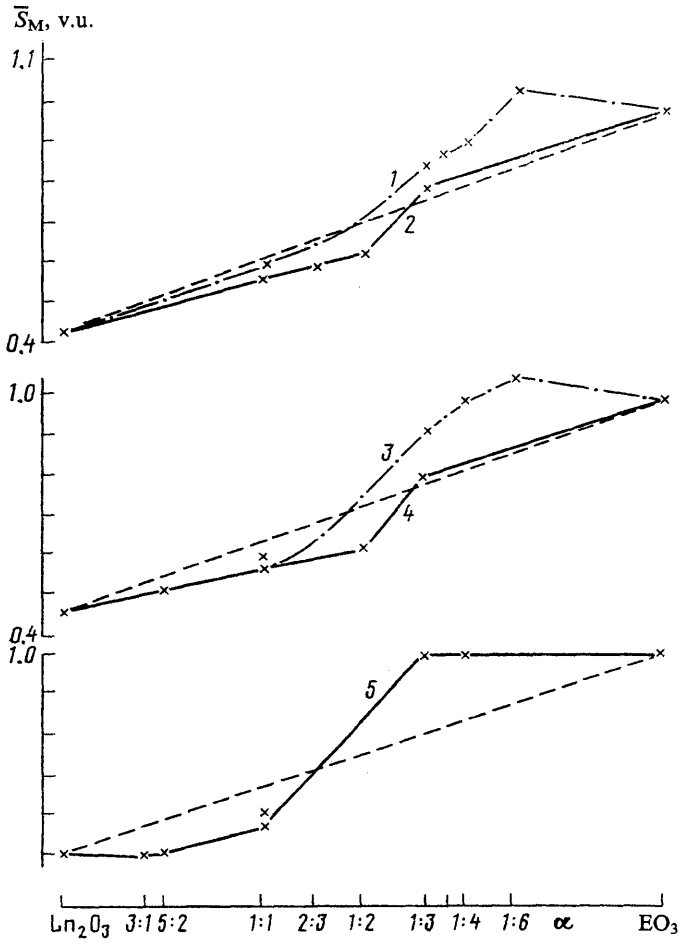


Figure 4. Variation of the quantities $\overline{S}_M$ with the oxygen index α in the structures of compounds formed in different systems: *1*, $Ce_2O_3-MoO_3$; *2*, $Nd_2O_3-WO_3$; *3*, $Sm_2O_3-MoO_3$; *4*, $Eu_2O_3-WO_3$; *5*, $Y_2O_3-WO_3$.

If the composition of the system components includes cations with very different electronegativities, then the relations considered usually becomes S-shaped (Fig. 4). On the other hand, in the case of salt systems of the type $M_2EO_4-L_2(EO_4)_3$, the curves are monotonic.

The dependence on α of the coordination numbers and the values of R_I^E averaged for cations of each kind are also smooth (Fig. 5):[104]

$$R_I^E = R_I^0 + K\ln\left[\left(\sum_{i=1}^{CN} S_i^0\right)\Big/ V_M\right],$$

where R_I^0 is the "statistical mean" value of the empirical parameter from Eqn. (8) and S_I^0 are the valence forces calculated with its aid.

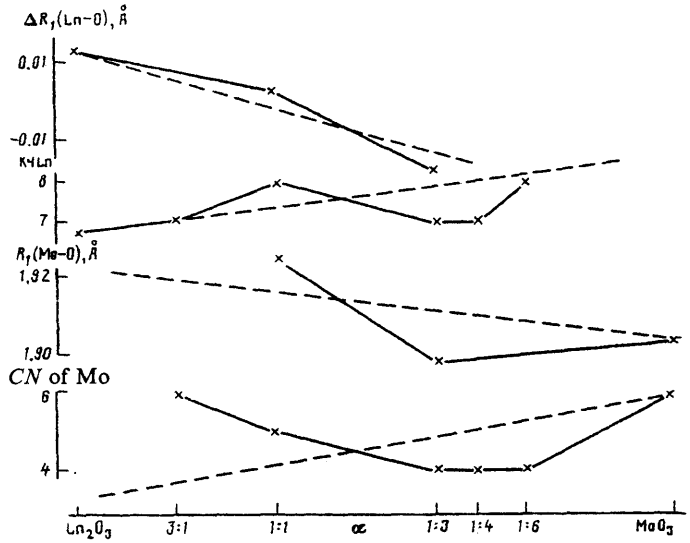


Figure 5. Dependence of the average coordination numbers and the values of R_I in the structures of compounds of the lanthanides in the middle of the series (molybdates) on the oxygen index.

Presumably the curves illustrated in Figs. 4 and 5 reflect the competition between the cations for the fraction of bond electron density supplied by the anions. It therefore appears useful to consider jointly the results obtained using both bond valence force models as well as other methods of theoretical and experimental chemistry for a wide range of systems. This might promote a more clear-cut establishment of the limits of applicability of the valence force model which has a high predictive power. For example, by introducing hypotheses concerning the alternation of cations and concerning the intercationic distances in the Nd_2MoO_6 structure, it proved possible to determine theoretically the geometrical characteristics of the NdO_8 and MoO_4 polyhedra with approximately the same accuracy as in the experiment.[51]

In our view, the data described in this review will undoubtedly prove useful in the computer modelling of the structure of inorganic oxide compounds.

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