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Short-Range Order and Superstructures of Ternary Oxides AMO_2, A_2MO_3 and A_5MO_6 of Monovalent A and Multivalent M Metals Related to the NaCl Structure

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Abstract

Ternary oxides AMO_2, A_2MO_3 and A_5MO_6 with monovalent A and tri-, tetra- or hepta-valent M metals can exhibit order/disorder transitions with about 20 superstructures of the NaCl lattice. Some structures can be related to AM, A_2M and A_5M alloys with a larger distortion of the lattice due to stronger interactions between metal atoms. In ternary oxides about 30 short-range order configurations are selected for the first, second and third shell of metal atoms in applying Pauling's electrovalence rule. Stable configurations are characterized by the strength of Coulomb interactions and by a high point symmetry of the M atoms. Mainly disordered ternary oxides can vary stoichiometrically with a frequent occurrence of vacancies or with partial occupation of tetrahedral interstices by A atoms.

I. Introduction

Many ternary oxides with the composition AMO_2, A_2MO_3 and A_5MO_6 of monovalent A and tri-, tetra- or hepta-valent M metals exhibit crystal structures closely related to the NaCl structure. The A and M metal atoms are distributed randomly or are in an ordered superstructure occupying Na positions, while O atoms are on the Cl positions. This might be due to the stability of the NaCl structure for octahedrally coordinated A and M atoms at 1:1 metal/oxygen ratio and the Coulomb interactions in ternary oxides. Pauling's electrovalence rule is strictly held only for these particular compositions. The sum of the electrovalencies z/n (z = charge, n = coordination number) of the six nearest A and M neighbours of each O atom should be equal to the charge of ionic oxygen:

$$\tfrac{1}{2}A^{+1}M^{+3}O_2 = A^{+1}_{3/6}M^{+3}_{3/6}O,\ \sum z/n = 3 \times \tfrac{1}{6} + 3 \times \tfrac{3}{6} = 2;$$

$$\tfrac{1}{3}A_2^{+1}M^{+4}O_3 = A^{+1}_{4/6}M^{+4}_{2/6}O,\ \sum z/n = 4 \times \tfrac{1}{6} + 2 \times \tfrac{4}{6} = 2;$$

$$\tfrac{1}{6}A_5^{+1}M^{+7}O_6 = A^{+1}_{5/6}M^{+7}_{1/6}O,\ \sum z/n = 5 \times \tfrac{1}{6} + 1 \times \tfrac{7}{6} = 2.$$

The electrovalency of oxygen is compensated only when it has either three trivalent, two tetravalent or one heptavalent besides the monovalent metal atoms as nearest neighbours.

II. Short-range order models

Short-range order has been investigated for f.c.c. alloys (Tanner & Leamy, 1974) and can be compared with the ternary oxides of this investigation. In many cases alloys of metals A and M with composition AM, A_2M or A_5M show the same or closely related superstructures as the metal atoms of AMO_2, A_2MO_3 or A_5MO_6 ternary oxides. The short-range order configurations of the disordered alloys may usually be related to the ordered superstructures (Clapp, 1971). Because of the large variety of the short-range order configurations and the weak interactions between the metal atoms, the nearest neighbours only are considered for short-range ordering of alloys. In this investigation short-range order configurations favoured by somewhat stronger Coulomb interactions in ternary oxides are selected. The location of the highly charged M atoms in the first three shells around each M atom with the translational vectors $\mathbf{T}_1 = (a/2\ a/2\ 0)$, $\mathbf{T}_2 = (a\ 0\ 0)$ and $\mathbf{T}_3 = (a\ a/2\ a/2)$ are considered. According to Pauling's rule the variety of short-range order con-

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figurations can be restricted to approximately 30 by a structure model (Figs. 1–3). These are marked by different letters when the next-nearest neighbours at $\mathbf{T}_1 = (a/2\ a/2\ 0)$ and $\mathbf{T}_2 = (a\ 0\ 0)$ are different, as shown in the inner circles of Figs. 1 and 2. The numbers after these letters indicate different distributions of M atoms at $\mathbf{T}_3 = (a\ a/2\ a/2)$. At the composition A_5MO_6 the M atoms do not have M neighbours at $\mathbf{T}_1 = (a/2\ a/2\ 0)$ and $\mathbf{T}_2 = (a\ 0\ 0)$, if Pauling's rule is applied. Configurations which can be obtained by a mirror plane from one of those shown are not included. For A and B configurations of A_2MO_3 the M atoms can be at the centre of different screw axes as shown in Fig. 2. In the known ordered structures M atoms with left- and right-handed screws occur in a 1:1 ratio. A possible exception would be a single crystal with a $B3$ configuration, where all M atoms can have either the R- or L-form.

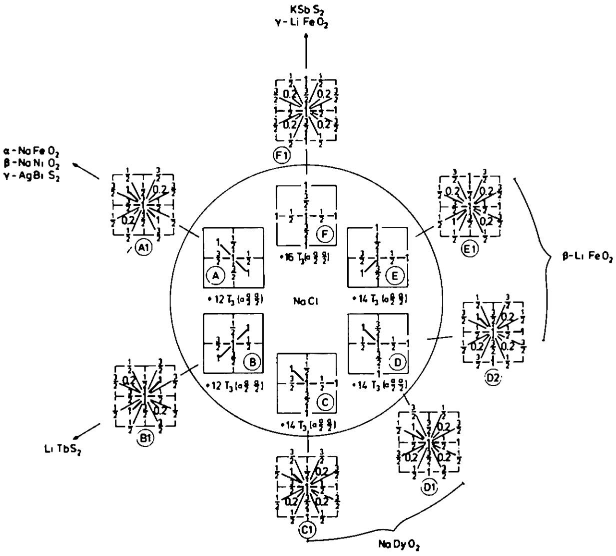


Fig. 1. Short-range order in ternary oxides AMO_2 with distribution of M atoms at $\mathbf{T}_1 = (a/2\ a/2\ 0)$, $\mathbf{T}_2 = (a\ 0\ 0)$ and $\mathbf{T}_3 = (a\ a/2\ a/2)$ in eight NaCl cells.

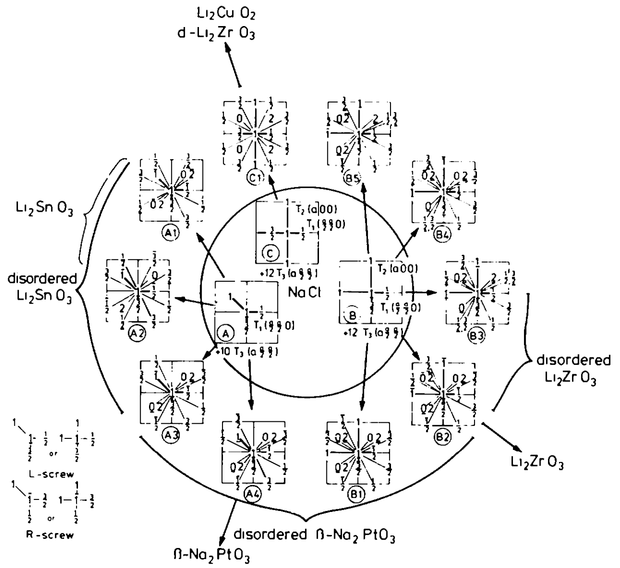


Fig. 2. Short-range order in ternary oxides A_2MO_3 with distribution of M atoms at $\mathbf{T}_1 = (a/2\ a/2\ 0)$, $\mathbf{T}_2 = (a\ 0\ 0)$ and $\mathbf{T}_3 = (a\ a/2\ a/2)$ in eight NaCl cells. Enantiomorphic configurations are indicated by bars above or below the positional number as shown at lower left.

The different short-range order configurations characterized by the number of neighbouring M atoms $[\mathbf{T}_i]$ at $\mathbf{T}_1 = (a/2\ a/2\ 0)$, $\mathbf{T}_2 = (a\ 0\ 0)$ and $\mathbf{T}_3 = (a\ a/2\ a/2)$ and by the point symmetry of the central M atom with the full international symbols are given in Table 1. The lowering of the point symmetry of the disordered NaCl structure $\frac{4}{m}\bar{3}\frac{2}{m}$ is important for the kind of lattice distortion in ordered structures. From the number of neighbouring M atoms, the short-range order parameter α, the translational vector ratio r and a Madelung factor for Coulomb interactions $MF^{*}_{(3)}$ can be obtained as outlined below.

Cowley & Warren have defined short-range order parameters α_i, which can be obtained from the diffuse intensity distribution (Warren, 1969):

$$\alpha_i = 1 - p_i^A/x_A.$$

p_i^A is the probability of finding an A atom at the translation $\mathbf{T}_i$ of an M atom and has the values $(12 - [\mathbf{T}_1])/12$, $(6 - [\mathbf{T}_2])/6$ and $(24 - [\mathbf{T}_3])/24$ for the first, second and third shell, respectively. x_A is the metal-atom fraction of A atoms in the compound and is 1/2 in AMO_2, 2/3 in A_2MO_3 and 5/6 in A_5MO_6. The short-range order parameters thus obtained are listed in Table 1. α_1, α_2 and α_3 are correlated by the equations $4\alpha_1 + \alpha_2 = -1$ (Brunel, de Bergevin & Gondrand, 1972) and $\alpha_1 + \alpha_3 = 0$, if Pauling's rule is applied. The negative values of α_1 and in some cases also of α_2

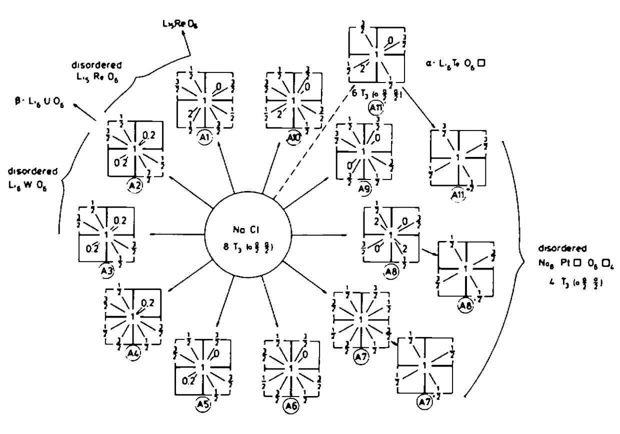


Fig. 3. Short-range order in ternary oxides A_5MO_6 and related compounds with distribution of M atoms at $\mathbf{T}_3 = (a\ a/2\ a/2)$ in eight NaCl cells.

indicate a preference for nearest unlike neighbours in the first or second shell due to the repulsive Coulomb interactions of the more highly charged M atoms. Positive α_1 values would indicate a tendency for clustering with a preference of nearest like neighbours. Pauling's rule would be violated for a completely random distribution in the NaCl structure with $\alpha_i = 0$ because of the relation $4\alpha_1 + \alpha_2 = -1$.

Ordered structures with primarily ionic bonding can also be compared by their Madelung lattice energy. The structure having the highest energy is the most probable one, provided other contributions to the lattice energy, such as covalency and Born repulsion energy, do not differ appreciably in closely related structures. The Madelung lattice energy E_M of an undistorted NaCl-type lattice depends on the Madelung factor MF and the NaCl lattice constant a_0 (in Å):

$$E_M = 1{\cdot}3892\ (2MF/a_0) \times 10^6\ \text{(J/mol)}.$$

MF can be obtained from a fast convergence by the Evjen method (Tosi, 1964) where the crystal is split into nearly neutral cubes of edge length a_0, $2a_0$ or $3a_0$ for the first, second or third approximation. The charge distribution for atoms at the faces, edges and corners of the cube is considered to be 1/2, 1/4 and 1/8, respectively. A cube with the edge length $2a_0$ gives to a close approximation the value for NaCl (MF = 1·747565) (Tosi, 1964)

$$MF_{(2a)} = \frac{6}{1} - \underset{\mathbf{T}_1}{\frac{12}{\sqrt{2}}} + \frac{8}{\sqrt{3}} - \underset{\mathbf{T}_2}{\left(\frac{6}{2}\right)\Big/2} + \left(\frac{24}{2}\right)\Big/\sqrt{5} - \underset{\mathbf{T}_3}{\left(\frac{24}{2}\right)\Big/\sqrt{6}} - \underset{\mathbf{T}_4}{\left(\frac{12}{4}\right)\Big/\sqrt{8}} + \left(\frac{24}{4}\right)\Big/3 - \underset{\mathbf{T}_5}{\left(\frac{8}{8}\right)\Big/\sqrt{12}} = 1{\cdot}752.$$

Table 1. *Point symmetry (full international symbol) of M atoms, number of* $\mathbf{T}_1$, $\mathbf{T}_2$ *and* $\mathbf{T}_3$ *vectors to neighbouring M atoms and different parameters for characterization of the short-range order in* AMO_2, A_2MO_3 *and* A_5MO_6 *ternary oxides*

For the three-dimensionally disordered NaCl structure values on application of Pauling's rule are added in brackets.

Composition	Short-range order (Figs. 1–3)	Point symmetry of M	Number of M atoms $[\mathbf{T}_i]$ at $\mathbf{T}_1$	$\mathbf{T}_2$	$\mathbf{T}_3$	Short-range order parameter α_i α_1	α_2	α_3	$r = \frac{[\mathbf{T}_1]}{[\mathbf{T}_1] + [\mathbf{T}_2]}$	$MF^*_{(3)}$
AMO_2	(NaCl)	$\frac{4}{m}\bar{3}\frac{2}{m}$	6 (4·8	3 2·4	12 14·4	0 –0·2	0 –0·2	0 0·2	0·67 0·67	0 –0·068)
	$A1, B1$	$\bar{3}\frac{2}{m}$	6	0	12	0	–1	0	1	–0·101
	$C1, D1, D2$	2	5	2	14	–0·167	–0·333	0·167	0·71	–0·074
	$E1$	m	5	2	14	–0·167	–0·333	0·167	0·71	–0·074
	$F1$	$\bar{4}2m$	4	4	16	–0·333	0·333	0·333	0·5	–0·047
A_2MO_3	(NaCl)	$\frac{4}{m}\bar{3}\frac{2}{m}$	4 (2·4	2 1·2	8 11·2	0 –0·2	0 –0·2	0 0·2	0·67 0·67	0 –0·137)
	$A1$–$A4$	2	3	0	10	–0·125	–0·5	0·125	1	–0·161
	$B1$–$B3$	2	2	2	12	–0·25	0	0·25	0·5	–0·120
	$B4, B5$	1	2	2	12	–0·25	0	0·25	0·5	–0·120
	$C1$	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	2	2	12	–0·25	0	0·25	0·5	–0·120
A_5MO_6	(NaCl)	$\frac{4}{m}\bar{3}\frac{2}{m}$	2 (0	1 0	4 8	0 –0·2	0 –0·2	0 0·2	0·67	0 –0·342)
	$A1, A4, A9, A10$	2	0	0	8	–0·2	–0·2	0·2	–	–0·342
	$A2$	$\frac{2}{m}$	0	0	8	–0·2	–0·2	0·2	–	–0·342
	$A3$	222	0	0	8	–0·2	–0·2	0·2	–	–0·342
	$A5, A6$	1	0	0	8	–0·2	–0·2	0·2	–	–0·342
	$A7$	422	0	0	8	–0·2	–0·2	0·2	–	–0·342
	$A8$	$\bar{4}$	0	0	8	–0·2	–0·2	0·2	–	–0·342
A_6MO_6	$A11'$	$\bar{3}$	0	0	6	–0·167	–0·167	0·125	–	–0·424
A_8MO_6	$A7'$	4	0	0	4	–0·125	–0·125	0·063	–	–0·506
	$A8'$	$\bar{4}$	0	0	4	–0·125	–0·125	0·063	–	–0·506
	$A11''$	$\bar{1}$	0	0	4	–0·125	–0·125	0·063	–	–0·506

The atoms at greater distance have less influence on *MF*. In this investigation the stabilization of a short-range order configuration by Coulomb interactions between the higher charged *M* atoms in the first, second and third shell will be considered by their contribution $MF'_{(3)}$ at $\mathbf{T}_1$, $\mathbf{T}_2$ and $\mathbf{T}_3$:

$$MF'_{(3)} = -[\mathbf{T}_1]/\sqrt{2} - [\mathbf{T}_2]/4 - [\mathbf{T}_3]/\sqrt{24}.$$

These values can be treated in a way similar to α_i values in the equation

$$MF^*_{(3)} = -1 + MF'_{(3)}/(\overline{MF'_{(3)}}\, x_M).$$

$\overline{MF'_{(3)}} = -14{\cdot}884$ is obtained, when all metal positions at $\mathbf{T}_1$, $\mathbf{T}_2$ and $\mathbf{T}_3$ are occupied by *M* atoms; x_M is the atomic fraction of *M* atoms in the compound (without oxygen). The resulting $MF^*_{(3)}$ range from 0 for a random distribution of *M* atoms to -1 for a structure having strong short-range repulsive interactions with no *M* atoms at $\mathbf{T}_1$, $\mathbf{T}_2$ and $\mathbf{T}_3$. $[\mathbf{T}_2]$ and $[\mathbf{T}_3]$ depend on $[\mathbf{T}_1]$, if Pauling's rule is valid.

$$[\mathbf{T}_2] = 30 - 36x_A - 2[\mathbf{T}_1],$$

$$[\mathbf{T}_3] = 48(1 - x_A) - 2[\mathbf{T}_1].$$

In that case $MF^*_{(3)}$ can be related to α_1 by

$$MF^*_{(3)} = (1 - 1/x_M)(0{\cdot}162\alpha_1 + 0{\cdot}101).$$

The α_1 values for the allowed short-range order configurations (Table 1) are within the range $-0{\cdot}333 \leq \alpha_1 \leq 0$ for AMO_2, $-0{\cdot}25 \leq \alpha_1 \leq -0{\cdot}125$ for A_2MO_3 and $\alpha_1 = -0{\cdot}2$ for A_5MO_6. Therefore the $MF^*_{(3)}$ values may vary only within a small range. The short-range order configurations with the largest $MF^*_{(3)}$ value (*F*1 for AMO_2 and *B*1–*C*1 for A_2MO_3) exhibit the highest Coulomb energy. The Madelung lattice energies of different crystal structures are equal if the *M* atoms have the same $MF^*_{(3)}$ values and no distortion of the lattice. For different $MF^*_{(3)}$ values it varies only by 1·9% for AMO_2 and by 1·3% for A_2MO_3 compounds.

The ratio $r = [\mathbf{T}_1]/([\mathbf{T}_1] + [\mathbf{T}_2])$ considers only the translation to the first and second shell of *M* neighbours. For random distribution of *M* atoms at $\mathbf{T}_1$ and $\mathbf{T}_2$, $r = 0{\cdot}67$. In Fig. 4 the volume of one formula unit of different modifications of Na_2PtO_3 can be related to *r*. The volume decreases with increasing *r* values (Hauck, 1977). By the decrease of lattice constants, ordered structures with smaller Madelung factors, *MF*, can gain Coulomb energy E_M. Three-dimensionally disordered γ-Na_2PtO_3 and two-dimensionally disordered *d*-α-Na_2PtO_3 and *d*-β-Na_2PtO_3 exhibit volume expansions as expected for random distribution of *M* atoms with the different configurations shown in Fig. 2. For a three-dimensionally random distribution of different configurations with an average of $r = 0{\cdot}67$, $\alpha_1 = \alpha_2 = -0{\cdot}2$, $\alpha_3 = 0{\cdot}2$ and $MF^*_{(3)} = (1 - 1/x_M)$, 0·068 would be obtained from the $[\mathbf{T}_i]$ values given in Table 1.

III. Crystal structures of ordered AMO_2, A_2MO_3 and A_5MO_6 ternary oxides

Structural data of ternary oxides related to the NaCl structure are given in Table 2, which also includes some theoretical variations in crystal structures. These are marked by Roman numbers. Disordered structures are designated by *d*. The crystal structures of the ternary oxides are characterized by the short-range order configuration of the *M* atoms, their space group and the point symmetry of *M* atoms, the number *z* of formula units in the unit cell and the lattice constants of the undistorted cell in a_0 units of the NaCl lattice. From this compilation one may select the stable short-range order configurations occurring in ordered structures and the less stable configurations, which occur in disordered structures. The configurations with very low point symmetry such as *B*4 and *B*5 in A_2MO_3 or *A*5, *A*6 in A_5MO_6 seem to be less favoured, even in disordered systems, because of the difficulty of forming a three-dimensional lattice with these configurations. Other configurations such as *A*7, *A*8 and *A*11′ in A_5MO_6 seem to occur in the closely related defect structures *A*7′, *A*8′ and *A*11″, where some positions of neighbouring *M* atoms are not occupied by *M* atoms (Fig. 3).

In most ordered structures the point symmetry of the *M* atoms is identical to those of the short-range order configurations. In β-$NaNiO_2$ and for one half of the Bi atoms in γ-$AgBiSe_2$ the symmetry of the *A*1 configuration is lowered from $\bar{3}\frac{2}{m}$ to $\frac{2}{m}$ and $3m$, respectively, and in the *F*1 configuration of $KSbS_2$ from $\bar{4}2m$ to 2. Also, for the *B*2 configuration of Zr atoms in Li_2ZrO_3 (III) the point symmetry is lowered to 1 and in the *A*2 configuration of β-Li_6UO_6 to $\bar{1}$. The reason for

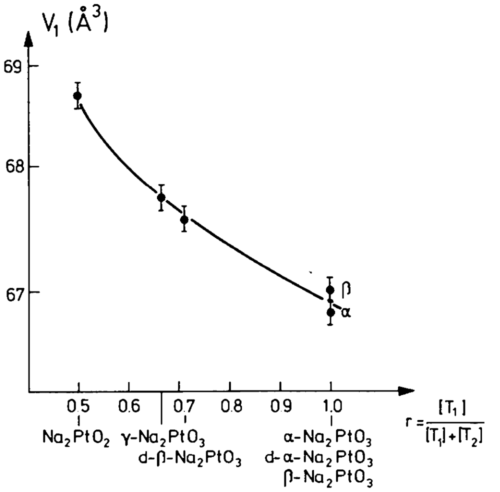


Fig. 4. Volume per formula unit V_1 of Na_2PtO_3 modifications with different ratios *r* of $\mathbf{T}_1$ and $\mathbf{T}_2$ translations between Pt atoms (α-Na_2PtO_3 with the Li_2SnO_3(III) structure, γ-Na_2PtO_3 with the *d*-Na_2CeO_3 structure and Na_2PtO_2 with the Li_2CuO_2 structure).

Table 2. *Space group, point symmetry of M atoms, number of formula units z, short-range order configuration and lattice constants of undistorted cell in units of a_0 of the* NaCl *structure for AMO_2, A_2MO_3 and A_5MO_6 ternary oxides*

Structure	Space group	Point symmetry of M	z	Reference	Short-range order	Lattice constants of undistorted cell in units of a_0
d-α-LiFeO$_2$	$Fm3m$	$\frac{4}{m}\bar{3}\frac{2}{m}$	2	Wyckoff (1965)	A–F	$a = a_0$
α-NaFeO$_2$	$R\bar{3}m$	$\bar{3}\frac{2}{m}$	3 1	Wyckoff (1965)	$A1$	$a_{\mathrm{hex}} = \sqrt{0{\cdot}5}a_0$, $c_{\mathrm{hex}} = \sqrt{12}a_0$ $a_{\mathrm{rh}} = \sqrt{1{\cdot}5}a_0$, $\alpha = 33{\cdot}56°$
β-NaNiO$_2$	$C2/m$	$\frac{2}{m}$	2	Wyckoff (1965)	$A1$	$a,c = \sqrt{1{\cdot}5}a_0$, $b = \sqrt{0{\cdot}5}a_0$, $\beta = 109{\cdot}47°$
γ-AgBiSe$_2$	$P\bar{3}m1$	$\bar{3}\frac{2}{m}$, $3m$	3	Wyckoff (1965)	$A1$	$a = \sqrt{0{\cdot}5}a_0$, $c = \sqrt{12}a_0$
LiTbS$_2$	$Fd3m$	$\bar{3}\frac{2}{m}$	16	Plug & Prodan (1978)	$B1$	$a = 2a_0$
NaDyO$_2$	$C2/c$	2	8	Gondrand, Brunel & de Bergevin (1972)	$C1$, $D1$	$a = 2a_0$, $b = \sqrt{8}a_0$, $c = \sqrt{1{\cdot}5}a_0$, $\beta = 144{\cdot}74°$
β-LiFeO$_2$	$I4_1/amd$ (2 setting)	2,m	32	Brunel & de Bergevin (1968)	$D2$,$E1$	$a = \sqrt{8}a_0$, $c = 2a_0$
γ-LiFeO$_2$	$I4_1/amd$ (1 setting)	$\bar{4}2m$	4	Wyckoff (1965)	$F1$	$a = a_0$, $c = 2a_0$
KSbS$_2$	$C2/c$	2	4	Graf & Schäfer (1975)	$F1$	$a,b = \sqrt{2}a_0$, $c = \sqrt{1{\cdot}5}a_0$, $\beta = 125{\cdot}26°$
d-Na$_2$CeO$_3$	$Fm3m$	$\frac{4}{m}\bar{3}\frac{2}{m}$	4/3	Wyckoff (1965)	A–C	$a = a_0$
d-Li$_2$SnO$_3$	$R\bar{3}m$	$\bar{3}\frac{2}{m}$	2/3 2	Trömel & Hauck (1970)	$A1$–$A3$	$a_{\mathrm{rh}} = \sqrt{1{\cdot}5}a_0$, $\alpha = 33{\cdot}56°$ $a_{\mathrm{hex}} = \sqrt{0{\cdot}5}a_0$, $c_{\mathrm{hex}} = \sqrt{12}a_0$
d-β-Na$_2$PtO$_3$	$Immm$	$mm2$	2		$A3$, $A4$, $B1$, $B2$	$a = \sqrt{4{\cdot}5}a_0$, $b = \sqrt{0{\cdot}5}a_0$, $c = a_0$
d-Li$_2$ZrO$_3$	$R\bar{3}m$	$\bar{3}\frac{2}{m}$	1/3 1		$B2$, $B3$, $C1$	$a_{\mathrm{rh}} = \sqrt{0{\cdot}5}a_0$, $\alpha = 60°$ $a_{\mathrm{hex}} = \sqrt{0{\cdot}5}a_0$, $c_{\mathrm{hex}} = \sqrt{3}a_0$
Li$_2$SnO$_3$(I)	$C2/m$	2	4		$A3$	$a,c = \sqrt{1{\cdot}5}a_0$, $b = \sqrt{4{\cdot}5}a_0$, $\beta = 109{\cdot}47°$
Li$_2$SnO$_3$(II)	$P3_112$	2	6		$A1$, $A2$	$a = \sqrt{1{\cdot}5}a_0$, $c = \sqrt{12}a_0$
Li$_2$SnO$_3$(III)	$C2/c$	2	8	Wyckoff (1965)	$A1$, $A2$	$a = \sqrt{1{\cdot}5}a_0$, $b = \sqrt{4{\cdot}5}a_0$, $c = \sqrt{5{\cdot}5}a_0$, $\beta = 100{\cdot}02°$
β-Na$_2$PtO$_3$(I)	$Fddd$	2	16	Urland & Hoppe (1972)	$A4$	$a = \sqrt{18}a_0$, $b = \sqrt{2}a_0$, $c = 2a_0$
β-Na$_2$PtO$_3$(II)	$Cccm$	2	16		$A3$, $A4$	$a = 2a_0$, $b = \sqrt{2}a_0$, $c = \sqrt{18}a_0$
Li$_2$ZrO$_3$(I) Li$_2$CuO$_2$	$Immm$	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	2	Urland & Hoppe (1972)	$C1$	$a = \sqrt{4{\cdot}5}a_0$, $b = \sqrt{0{\cdot}5}a_0$, $c = a_0$
Li$_2$ZrO$_3$(II)	$P3_112$	2	3		$B3$	$a = \sqrt{1{\cdot}5}a_0$, $c = \sqrt{3}a_0$
Li$_2$ZrO$_3$(III)	Cc	1	4	Dittrich & Hoppe (1969)	$B2$	$a,c = \sqrt{1{\cdot}5}a_0$, $b = \sqrt{4{\cdot}5}a_0$, $\beta = 109{\cdot}47°$
Li$_2$ZrO$_3$(IV)	$C2/c$	2	4		$B2$	$a,c = \sqrt{1{\cdot}5}a_0$, $b = \sqrt{4{\cdot}5}a_0$, $\beta = 109{\cdot}47°$
d-Li$_2$Mg$_3$SnO$_6$	$Fm3m$	$\frac{4}{m}\bar{3}\frac{2}{m}$	2/3	Hauck (1970*b*)	$A1$–$A10$	$a = a_0$
d-Li$_5$ReO$_6$	$R\bar{3}m$	$\bar{3}\frac{2}{m}$	1/3 1		$A1$, $A2$	$a_{\mathrm{rh}} = \sqrt{1{\cdot}5}a_0$, $\alpha = 33{\cdot}56°$ $a_{\mathrm{hex}} = \sqrt{0{\cdot}5}a_0$, $c_{\mathrm{hex}} = \sqrt{12}a_0$
d-Li$_6$WO$_6$	$Immm$	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	1	Hauck (1969*a*)	$A2$, $A3$	$a = \sqrt{4{\cdot}5}a_0$, $b = \sqrt{0{\cdot}5}a_0$, $c = a_0$
Li$_5$ReO$_6$(I)	$C2/m$	$\frac{2}{m}$	2		$A2$	$a,c = \sqrt{1{\cdot}5}a_0$, $b = \sqrt{4{\cdot}5}a_0$, $\beta = 109{\cdot}47°$
Li$_5$ReO$_6$(II)	$P3_112$	2	3	Hauck (1968)	$A1$	$a = \sqrt{1{\cdot}5}a_0$, $c = \sqrt{12}a_0$
Li$_5$ReO$_6$(III)	$C2/c$	2	4		$A1$	$a = \sqrt{1{\cdot}5}a_0$, $b = \sqrt{4{\cdot}5}a_0$, $c = \sqrt{5{\cdot}5}a_0$, $\beta = 100{\cdot}02°$

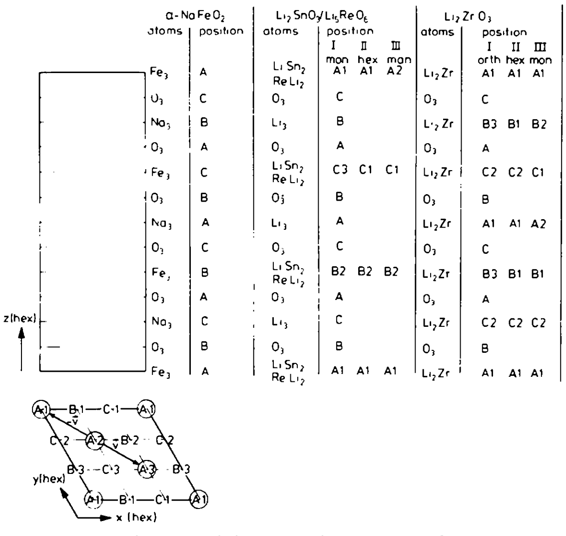
Table 2 (*cont.*)

Structure	Space group	Point symmetry of M	z	Reference	Short-range order	Lattice constants of undistorted cell in units of a_0
Li_6WO_6(I)	*Fddd*	222	8		$A3$	$a = \sqrt{18}a_0, b = \sqrt{2}a_0, c = 2a_0$
Li_6WO_6(II)	*Cccm*	$\frac{2}{m}$, 222	8		$A2, A3$	$a = 2a_0, b = \sqrt{2}a_0, c = \sqrt{18}a_0$
β-Li_6UO_6	$P\bar{1}$	$\bar{1}$	1	Hauck & Rosenhauer (1976)	$A2$	$a,b,c = \sqrt{1\cdot5}a_0, \alpha = 109\cdot47,$ $\beta = 120, \gamma = 80\cdot41°$
α-Li_6TeO_6	$R\bar{3}$	$\bar{3}$	3 1	Hauck (1970*c*)	$A11'$	$a_{hex} = \sqrt{3\cdot5}a_0, c_{hex} = \sqrt{2\cdot5}a_0$ $a_{rh} = \sqrt{1\cdot5}a_0, \alpha = 99\cdot59°$
d-Na_8PtO_6	$I4$	4	1	Hauck (1976*a*)	$A7', A8', A11''$	$a = \sqrt{2\cdot5}a_0, c = a_0$
Na_8PtO_6(I)	$P4$	4	2		$A7'$	$a = \sqrt{2\cdot5}a_0, c = 2a_0$
Na_8PtO_6(II)	$I\bar{4}$	$\bar{4}$	4		$A8'$	$a = \sqrt{5}a_0, c = 2a_0$
Na_8PtO_6(III)	$P\bar{1}$	$\bar{1}$	2		$A11''$	$a = \sqrt{3\cdot5}a_0, b = \sqrt{2\cdot5}a_0, c = 2a_0,$ $\alpha, \gamma = 90, \beta = 57\cdot69°$

lowering the point symmetry might be mainly covalency effects. The atom orbital symmetry in trivalent Ni, Bi or Sb is obviously different from the point symmetry of the short-range order configurations. Hexavalent uranium in β-Li_6UO_6 forms uranyl bonds, as has been concluded from the infrared spectra (Hauck & Rosenhauer, 1976). The experimentally determined symmetry for Li_2ZrO_3 (III) (Dittrich & Hoppe, 1969) indicates a distorted structure slightly different from the higher point symmetry of Zr in Li_2ZrO_3 (IV) (Table 2).

Some structures of alloys (Kozlov *et al.*, 1974; Tanner & Leamy, 1974; Pearson, 1972) can be compared with the superstructures of the metal atoms in ternary oxides. CuPt ($L1_1$) has the same superstructure as α-$NaFeO_2$, Pt_2Mo may be compared with the Li_2CuO_2 structure. CuAu ($L1_0$), $ZrGa_2$ and $HfGa_2$ exhibit an ordering which is not permitted by Pauling's rule for compounds with Coulomb interactions. For CuAu, however, intermediate antiphase domain structures were observed at elevated temperatures with variation in domain boundary between $M = 1$ and $6a_0$ (Kozlov *et al.*, 1974). For domain boundaries with $M = a_0$ the CuAu structure is identical to the metal-atom ordering in γ-$LiFeO_2$. The ordering in the Ni_4Mo structure can be compared with the defect structure of disordered Na_8PtO_6, where Pt atoms occupy randomly 50% of the Mo positions of Ni_4Mo as is discussed in § IV. The crystal structures of WAl_5 and seemingly also of $MoAl_5$ can be related to the Li_5ReO_6 structure (Fig. 5) with alternating Al_2W (or Al_2Mo) and Al_3 layers. In $MoAl_5$, however, the layers form hexagonal close packing in the sequence $A1B$ $A2B$ $A3B$ with Mo atoms of Al_2Mo layers at $A1$, $A2$ and $A3$ positions. In the WAl_5 structure the layers are stacked in the order $A2B$ $A3C$ with W atoms in WAl_2 layers alternating on $A2$ and $A3$ positions. The $MoAl_5$ structure can be related to the Li_8SnO_6 structure (Trömel & Hauck, 1969) with some additional Li atoms on tetrahedral interstices. At the composition A_5MO_6 a Li_5ReO_6 with a h.c.p. of layers would have a lower Madelung lattice energy than c.c.p. Li_5ReO_6 (Hauck, 1970*c*). Ordered alloys with superstructures of the f.c.c. lattice occur also at the ratio A_3M, A_4M, *etc.* but cannot be compared to oxides. The compositions A_3MO_4, A_4MO_5, *etc.* are not allowed by Pauling's rule.

The crystal structures of $BaSnS_2$ (Iglesias & Steinfink, 1973) and $NaAsS_2$ (Iglesias, Zúñiga & Nowacki, 1977) can be related to monoclinic distorted NaCl lattices, but with a short-range ordering of Sn or As atoms as in the CuAu ($L1_0$) structure. The sulphides are supposed to have stronger covalent bonding and less Coulomb interactions, because of the easy polarizability of the larger S atoms. $NaMnO_2$



α-$NaFeO_2$ atoms	position	Li_2SnO_3/Li_5ReO_6 atoms	position I mon	II hex	III mon	Li_2ZrO_3 atoms	position I orth	II hex	III mon
Fe_3	A	$LiSn_2$ $ReLi_2$	A1	A1	A2	Li_2Zr	A1	A1	A1
O_3	C	O_3	C			O_3	C		
Na_3	B	Li_3	B			Li_2Zr	B3	B1	B2
O_3	A	O_3	A			O_3	A		
Fe_3	C	$LiSn_2$ $ReLi_2$	C3	C1	C1	Li_2Zr	C2	C2	C1
O_3	B	O_3	B			O_3	B		
Na_3	A	Li_3	A			Li_2Zr	A1	A1	A2
O_3	C	O_3	C			O_3	C		
Fe_3	B	$LiSn_2$ $ReLi_2$	B2	B2	B2	Li_2Zr	B3	B1	B1
O_3	A	O_3	A			O_3	A		
Na_3	C	Li_3	C			Li_2Zr	C2	C2	C2
O_3	B	O_3	B			O_3	B		
Fe_3	A	$LiSn_2$ $ReLi_2$	A1	A1	A1	Li_2Zr	A1	A1	A1

Fig. 5. Hexagonal or pseudohexagonal structures of α-$NaFeO_2$ and several structural variants of Li_2SnO_3, Li_5ReO_6 and Li_2ZrO_3. For Li_2Re and Li_2Zr layers the positions of Re and Zr atoms, for $LiSn_2$ Li atoms are specified. Li_2SnO_3(III) and Li_2ZrO_3(III) are the observed ordered structures.

forms a β-modification where the O atoms have either two or four nearest Mn neighbours (Hoppe, Brachtel & Jansen, 1975). α-$NaMnO_2$ crystallizes in the β-$NaNiO_2$ structure with three Mn neighbours to each O atom, in accordance with Pauling's rule.

There are several compounds with the deficit NaCl structure, where Na or Cl or both positions exhibit vacancies (Wyckoff, 1965). Ordered distributions of vacancies could be obtained for $\mathrm{Pd}D_{0\cdot5}$ (Anderson, Carlile, Ross & Wilson, 1979) and $\mathrm{Pd}D_{0\cdot8}$ (Ellis, Satterthwaite, Mueller & Brun, 1979). The ordered defects □ in the D sublattice can be correlated to Fe or Pt atoms of the γ-$LiFeO_2$ and d-Na_8PtO_6 structures by the formula γ-$\mathrm{LiFeO_2} \hat{=} D\,\square\,\mathrm{Pd_2} = \mathrm{Pd}D_{0\cdot5}$ and d-$\mathrm{Na_8Pt}\,\square\,\mathrm{O_6}\,\square_4 \hat{=} D_8\,\square_2\,\mathrm{Pd_{10}} = 10\mathrm{Pd}D_{0\cdot8}$. Similarly, the carbon vacancies of Ti_2C and V_6C_5 are ordered as Tb or Re atoms of $LiTbS_2$, Li_5ReO_6(II) and Li_5ReO_6(III) structures.

Other binary compounds (Wyckoff, 1965) can be considered as deficient in A atoms: $\square\mathrm{CdCl_2} \hat{=}$ α-$NaFeO_2$, $\square\mathrm{TiO_2}$ (anatase) $\hat{=}$ γ-$LiFeO_2$, $\square_2\mathrm{AlCl_3} \hat{=} \mathrm{Li_2SnO_3}$(I) and $\square_2\mathrm{CrCl_3} \hat{=} \mathrm{Li_2SnO_3}$(II).

IV. Disordered structures and deviation from stoichiometry

Disorder of M atoms is most likely to be found in structures where M atoms can be shifted to neighbouring positions without much change in their configuration. This can be demonstrated by the Li_2SnO_3 structure, which can exhibit a one-dimensional disorder of layers (Trömel & Hauck, 1970). The projection of ABC positions of cubic close packing on the ab plane of the hexagonal or pseudo-hexagonal lattice and the occupation of the different sequences of A, B and C layers with Li, Sn and O atoms in the c direction is given in Fig. 5. The monoclinic Li_2SnO_3(III) structure represents the ordered form of Li_2SnO_3 (Wyckoff, 1965). The Li atoms of the fourth metal-atom layer of Li_2SnO_3(I) and of the sixth layer of Li_2SnO_3(II) are shifted from $C1$ to $C3$ and $A2$ to $A1$, respectively. The short-range order configuration of the Sn atoms stays unchanged $A1$ and $A2$ in Li_2SnO_3(II) and changes to the configuration $A3$ with the same Coulomb interaction parameter $MF^*_{(3)}$ in Li_2SnO_3(I) (Table 1). The Madelung energies of the three lattices are equal, if there is no distortion (Hauck, 1970c). One-dimensionally disordered Li_2SnO_3 could be obtained by reaction of Li_2CO_3 and SnO_2 at 1073–1273 K (Trömel & Hauck, 1970). The X-ray powder pattern exhibits asymmetric broadened reflexions for $h - k \neq 3n$ of hexagonal indexing. The structure factor of $LiSn_2$ layers must be multiplied by $\exp[\pm 2\pi i(h-k)/3]$, if the layers are shifted by $\pm\mathbf{v}(x = 1/3,\ y = -1/3)$. This factor equals one for reflexions with $h - k = 3n$. The disorder therefore can be analysed by comparison of the sharp $h - k = 3n$ and the broad $h - k \neq 3n$ reflexions. A similar disorder may occur in compounds with the Li_5ReO_6 structure (Hauck, 1968) (Fig. 5) and the closely related structures of β-Li_6ReO_6 (Hauck, 1969b) and Na_4XeO_6 (Hauck, 1970a). The powder pattern of many samples showed somewhat broadened $h - k \neq 3n$ reflexions which also had reduced integral intensities. β-Li_6ReO_6, obtained from ReO_2 and Li_2O within 10 h at 773 K, exhibited $h - k \neq 3n$ reflexions 1·6 times broader than $h - k = 3n$ reflexions. Approximately 20% disorder of Li_2Re layers could be estimated from ~40% decrease of the structure factor parameters. In other compounds such as Na_5IO_6 certain reflexions showed some deviation from hexagonal symmetry as occurs $e.g.$ in structure type III (Hauck, 1969c).

A similar disorder of layers could also occur in the Li_2ZrO_3 structure, but not in the α-$NaFeO_2$ structure (Fig. 5). Li_2ZrO_3 crystallizes in the Li_2ZrO_3(III) structure (Dittrich & Hoppe, 1969). Li_2ZrO_3(I) would already differ in the second Li_2Zr layer with Zr at $B3$ instead of the $B1$ position; Li_2ZrO_3(II) is different in the third layer with Zr at $A1$ instead of the $A2$ position.

Disordered structures were observed in β-Na_2PtO_3 (Hauck, 1976a) and Li_6WO_6 (Hauck, 1969a), which are closely related orthorhombic structures as shown in a projection net of the NaCl structure in Fig. 6. Ordered β-Na_2PtO_3 crystallizes in the structure type I (Urland & Hoppe, 1972). β-Na_2PtO_3(II) and Li_2SnO_3(I) are closely related structure models, where some Pt atoms are shifted by $\pm\mathbf{v}$. d-β-Na_2PtO_3 would be the disordered structure with a random occurrence of this translation at the different Pt positions. For Li_6WO_6 similar structures can be evaluated (Fig. 6). In Li_6WO_6(II) two W atoms are shifted by $\mathbf{v}$ compared with Li_6WO_6(I) without change of Madelung lattice energy (Hauck, 1970c). So far only the disordered structure d-Li_6WO_6 has been obtained. An additional broad reflexion can be indexed as 111 with the doubled cell constants of I or II. The intensity of this reflexion

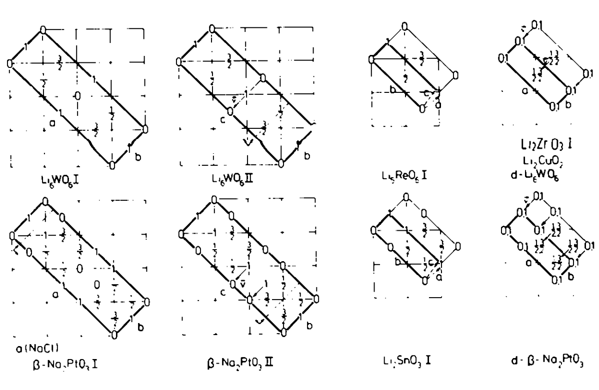


Fig. 6. Relationship between several structural variations of β-Na_2PtO_3 and Li_6WO_6. Positions of M atoms projected at NaCl structure cells.

increases with increasing fraction of $A3$ configuration, depending on time and temperature of annealing. d-Li_6WO_6 shows the same structure as Li_2CuO_2 or Li_2ZrO_3(I), however, with only half the Cu or Zr positions occupied by W. Na_2PtO_2 was reported as isomorphic to Li_2CuO_2 (Urland & Hoppe 1972). The powder pattern, however, exhibits broad additional reflexions, which can be indexed as 111 and 511 with the cell constants of the larger cell (I). This indicates that this compound may be described as a solid solution between Na_2PtO_2 and β-Na_2PtO_3 with the formula Na_2PtO_{3-x}.

Several compounds with a deviation from 1:1 metal/oxygen ratio were mentioned in the discussion above. For d-Li_6WO_6 and β-Li_6ReO_6 it is not known whether the additional Li atoms to A_5MO_6 are on tetrahedral interstices or if there are voids □ in the oxygen lattice similar to that in Li_2CuO_2□. Na_4□XeO_6 exhibits a deficiency of Na atoms. α-Li_6TeO_6□ can be considered with ordered voids at every seventh position of the oxygen packing (Fig. 7) (Hauck, 1970c). The Te atoms are at octahedral positions, whereas each Li atom has only five O atom neighbours. Because of the different composition the Te atoms have a different short-range order configuration $A11'$ with only six nearest Te neighbours at T_3 translations (Fig. 3). At 973 K and 22 × 10^8 Pa this compound forms a high-pressure modification with the β-Li_6ReO_6 structure, where all O atom positions are occupied (Hauck & Hirschberg, 1969). α-Li_6UO_6 forms a structure with similar lattice constants (Hauck, 1973), where the UO_6 octahedra are rotated by about 20° on the $\bar{3}$ axis as in the $TlSbF_6$ structure compared with the $KOsF_6$ structure (Wyckoff, 1965). In α-Li_6UO_6 the Li atoms are tetrahedrally coordinated by O atoms.

Na_8PtO_6 has a distorted NaCl superstructure with vacancies □ both in the metal and O atom positions according to the formula Na_8Pt□O_6□$_4$ (Hauck, 1976a). The ten metal and O atom positions of d-Na_8PtO_6 are in a body-centred tetragonal cell (Fig. 8). Each Pt atom has only four Pt neighbours at $\mathbf{T}_3 = (a\ a/2\ a/2)$, if only half of the Pt positions are occupied, as is outlined in Fig. 8 for some structure models of ordered superstructures I–III. The short-range order configurations $A7'$, $A8'$ and $A11''$ can be considered as deficient configurations of $A7$, $A8$ and $A11'$ (Fig. 3). It was impossible to obtain good Na_8PtO_6 samples for the study of superstructure ordering, because of the ready decomposition at elevated temperatures. In Na_8PtO_6(I) the unit cell would be two times, in (II) four times larger than that of d-Na_8PtO_6 (Table 2) with $c_{\text{tet.}}$ doubled. A partial order of these structure variances would exhibit diffuse reflexions for $l \neq 2n$ of the enlarged unit cell.

Three-dimensionally disordered structures with the diffraction pattern of the NaCl structure can be obtained at the composition AMO_2 (α-$LiFeO_2$ structure) (Wyckoff, 1965) A_2MO_3(Na_2CeO_3 structure) (Wyckoff, 1965) and A_5MO_6 ($Li_2Mg_3SnO_6$ structure) (Hauck, 1970b). It can be concluded from the relation $4\alpha_1 + \alpha_2 = -1$ and from the different Coulomb interaction factors $MF^*_{(3)}$ that these compounds do not have a completely random distribution of M atoms but short-range order configurations as given in Figs. 1–3 with a preference for those configurations which also occur in ordered structures. Short-range order in d-$Li_2Mg_3SnO_6$ and also in the disordered structures d-Li_6WO_6 and d-Na_8PtO_6 with the occurrence of isolated MO_6 octahedra was also suggested from infrared spectra (Hauck, 1970d). Isolated octahedra can be identified by ν_3 (F_{1u}) and ν_4 (F_{1u}) vibrations of cubic

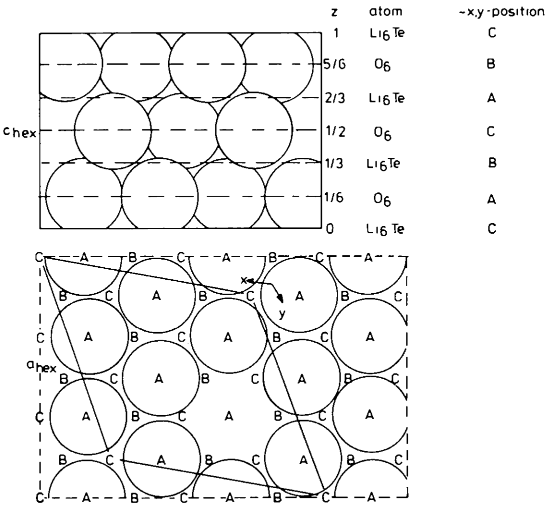
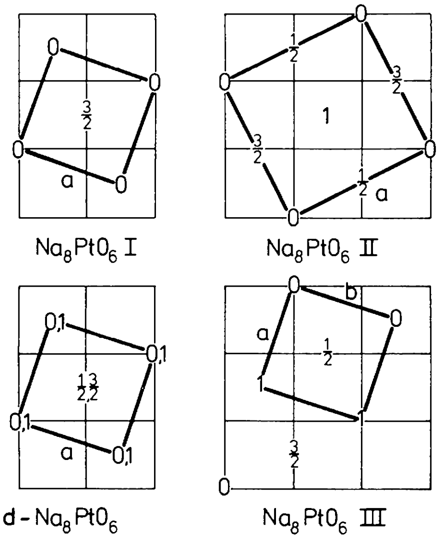


Fig. 7. Hexagonal cell of rhombohedral α-Li_6TeO_6□. Hexagonal layer of six O atoms and one void at A positions below. Sequence of O atoms and metal layers above.



Na_8PtO_6 I Na_8PtO_6 II d-Na_8PtO_6 Na_8PtO_6 III

Fig. 8. Some possible superstructures for disordered Na_8PtO_6. Positions of Pt atoms projected at NaCl structure cells.

symmetry and some splitting, if the octahedra are distorted with a lower point symmetry of the central M atom. In the similar structure of $K_5Mn(CN)_6$ (Hauck, 1976*b*), CN groups are located on Cl positions of the NaCl structure. Infrared spectra indicate that the Mn atoms are bound only to the C atoms. Therefore K atoms must be coordinated to N atoms around the isolated $Mn(CN)_6$ octahedra. In these compounds the translational vectors $[\mathbf{T}_i]$ and the related parameters α_i, r and $MF^*_{(3)}$ should be different from the values given in Table 1 for completely random distribution.

In some disordered systems like $LiReO_2$ (Pfeiffer, 1963) or $K_5Mn(CN)_6$ (Hauck, 1976*b*), densities smaller than the theoretical values were measured indicating defect structures. In $LiReO_2$ ~22% of the positions are not occupied, in $K_5Mn(CN)_6$ 6–17%. Deficiencies might easily occur in disordered structures, if the short-range order configurations do not fit to a three-dimensional lattice. The occurrence of defects can also explain the deviations from AMO_2, A_2MO_3 and A_5MO_6 stoichiometry. γ-Na_2PtO_3, for example, can react with additional Na_2O to give a product close to the composition Na_4PtO_4 (Hauck, 1976*a*). The diffraction lines of the NaCl structure are slightly shifted due to an increase of the lattice constant with increasing fraction of the larger Na atoms. In addition the integral line width increases to about $\theta \simeq 1°$ due to the increasing imperfection of the lattice. Defect structures can also be obtained if the valency of M is changed, as in $Na_{1{\cdot}8}Pr_{0{\cdot}8}La_{0{\cdot}2}O_{2{\cdot}8}$ (Zintl & Morawietz, 1940), where part of the trivalent La is substituted by tetravalent Pr, or in $LiFeO_2/Li_2TiO_3$ solid solution (Evans, 1976). Large deviations from stoichiometry were found in the solid solution of β-Li_3ReO_4/β-Li_4ReO_5/Li_5ReO_6 at 873 K (Pfeiffer, 1963, Hauck, 1979). They were obtained in the Li_5ReO_6 structure (Fig. 5) with the composition of Li_2Re layers changing to $Li_{1{\cdot}8}Re_{1{\cdot}2}$ in β-$Li_4Re^{+6}O_5$ and $Li_{1{\cdot}5}Re_{1{\cdot}5}$ in β-$Li_3Re^{+5}O_4$. In $Li_3\,(LiMg_{0{\cdot}67}Re^{+5}_{1{\cdot}33})O_6$ and $Li_4MgReO_6 \triangleq Li_3(LiMgRe)O_6$, some of the Li^+ ions are substituted by Mg^{2+} (Pfeiffer, 1963). A three-dimensionally disordered NaCl structure could be obtained for the composition α-Li_3ReO_4 (Pfeiffer, 1963) and α-Li_4WO_5 (Blasse, 1964; Hauck, 1974). Pauling's rule is strictly obeyed in α-Li_6TeO_6, Na_4XeO_6, Li_4MgReO_6 and $Li_2Mg_3SnO_6$. For Li_6WO_6, β-Li_6ReO_6, Na_8PtO_6, Na_4PtO_4, α-Li_4WO_5, β-Li_4ReO_5, α,β-Li_3ReO_4 and $Li_3(LiMg_{0{\cdot}67}Re_{1{\cdot}33})O_6$ it is only valid within a maximum deviation of ~1/6, especially in disordered structures where vacancies of the O atoms and some fraction of the Li atoms on tetrahedral positions may be considered.

V. Comparison between alloys and ternary oxides

It was shown in the preceding section that deviations from the stoichiometry AMO_2, A_2MO_3 and A_5MO_6 frequently occur in disordered systems and to much smaller extent in ordered structures. This behaviour is similar to that of alloy systems. In disordered ternary oxides, however, especially at small M content ($x_M <$ ~$0{\cdot}33$), defect structures are formed where some fraction of the NaCl lattice positions is not occupied. Because of the stronger metal–metal interactions in ternary oxides, neighbours at $\mathbf{T}_3 = (a\ a/2\ a/2)$ are also influenced and this leads to a reduced number of configurations. Disorder can easily give rise to deficiencies in the lattice, if the short-range order configurations do not fit to a three-dimensional lattice. There is also a larger variety of ordered structures in ternary oxides compared with alloys because of the different interactions. In most alloys the nearest M neighbours exhibit simple geometrical configurations with high point symmetry of the central M atom, which can be considered stable by geometrical considerations of packing spheres. In the $A1$ configurations of CuPt (or α-$NaFeO_2$), the nearest neighbours at $\mathbf{T}_1 = (a/2\ a/2\ 0)$ form a hexagon. The structure is typical for atoms with different sizes, which become ordered in alternating layers. In the CuAu structure four neighbours at $\mathbf{T}_1$ form a square, and six neighbours at $\mathbf{T}_2$ an octahedron. For the CuAu antiphase domain structure with $M = a_0$ (γ-$LiFeO_2$ structure) the four $\mathbf{T}_1$ neighbours form a tetrahedron and four neighbours at $\mathbf{T}_2$ a square. The B configuration of AMO_2 can be described as an octahedron of six nearest $\mathbf{T}_1$ neighbours elongated along a $\bar{3}$ axis. At A_2MO_3 or A_2M composition the M atoms form a triangle of three $\mathbf{T}_1$ neighbours in the A configuration and a cross with two $\mathbf{T}_1$ and two $\mathbf{T}_2$ neighbours in the C configuration (Pt_2Mo or Li_2CuO_2 structure). From these structures with simple geometrical arrangements only the B configuration of AM and the A configuration of A_2M were not observed in ordered alloys. All other configurations of Figs. 1–3 are more complex. Their stability can probably only be explained by the Coulomb interactions.

Stronger metal–metal interactions in ternary oxides can also be concluded from lattice distortions. Correction factors for lattice distortion were calculated for the lattice constants related to a_0 as given in Table 2, with a_0 for NaCl cells with equal volume. The sum of the absolute deviations from one of those correction factors was taken as a measure of the degree of lattice distortion. The lattice constants of tetragonal γ-$LiFeO_2$, *e.g.* $a = 4{\cdot}057$, $c = 8{\cdot}759$ Å, were related to the undistorted NaCl cell with $a_0 = (V/2)^{1/3} = 4{\cdot}162$ Å by $a = b = 0{\cdot}975a_0$ and $c = 1{\cdot}052 \times 2a_0$. The sum of Δ of the deviations of the correction factors $(1 - 0{\cdot}975) \times 2$ and $(1{\cdot}052 - 1)$ is equal to $0{\cdot}102$. The average Δ values for AMO_2 compounds is 0·10, for A_2MO_3 compounds 0·04 and for A_5MO_6 compounds 0·02, indicating smaller lattice distortions at decreasing M content of the oxides. For AM alloys ($\Delta = 0{\cdot}03$) and A_2M alloys ($\Delta = 0{\cdot}02$) the smaller values indicate the smaller interaction. For alloys with small M content such as A_5M the interaction seems to be too small for a formation of ordered alloys with cubic close packing because of the entropy at elevated temperatures, where A and M are mobile.

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Polarized X-ray Absorption and Double Refraction in Vanadyl Bisacetylacetonate

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Abstract

X-ray dichroism is observed in crystalline vanadyl bisacetylacetonate, $VO^{2+}.2(C_5H_7O_2)^-$, near the vanadium K edge in absorption experiments with linearly polarized synchrotron radiation. The Kossel structure is polarized as a result of the symmetries of molecular orbitals in this strongly anisotropic molecule. The extended X-ray absorption fine structure is polarized because of the difference in distance to the axial and equatorial oxygen neighbors. In this wavelength region, the anomalous-scattering terms and

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