Solid State Physical Chemistry

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Course Title	Solid State Physical Chemistry		Credit	3
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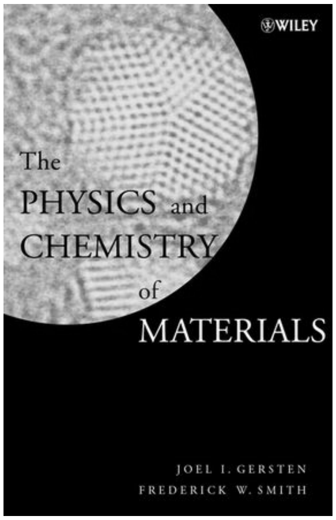
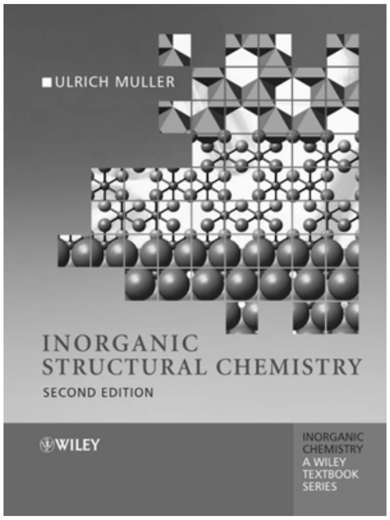
This subject teaches basic principles of solid state chemistry and shows how they can be used to describe the materials properties. In particular, the relationship between electronic structure, chemical bonding, and crystal structure is developed. The physical properties of the solid such as magnetic, electrical, optical, etc. are introduced and related to their electronic and crystal structure. Tentative topical coverage: Crystal structures, chemical bonding in solids (metallic, covalent, ionic), non-bonding electrons (d- and f-electrons, crystal field), defects in solids, electrical properties (metallic conductivity, semiconductivity, superconductivity, ionic conductivity, ferroelectricity, piezo electricity, optical properties (d- and f-electrons) and magnetic properties.

Grading	Attendance	Assignments	Mid-term exam	Final exam	Participation	Total
	10%	10%	10%	60%	10%	100%
	Remarks					

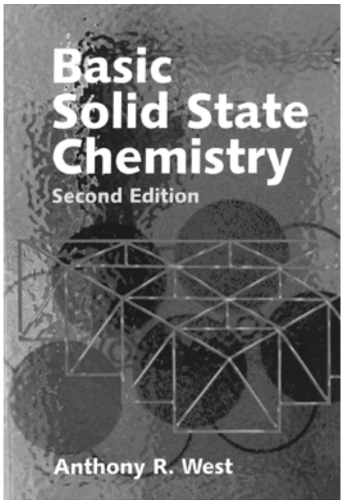
Lecture Plans	Week	Descriptions
	1	Introduction to Solid State Physical Chemistry
	2	Structure of Crystals
	3	Bonding in Solids
	4	Order and Disorder in Solids
	5	Phase Diagrams and Phase Transitions
	6	Metals and Alloys
	7	Covalent Solids
	8	Ionic Solids
	9	d and f Electrons in Solids
	10	Electrical and Thermal Properties of Materials
	11	Mechanical Properties of Materials
	12	Optical Properties of Materials
	13	Magnetic Properties of Materials
	14	Thin Films
	15	Nanostructured Materials

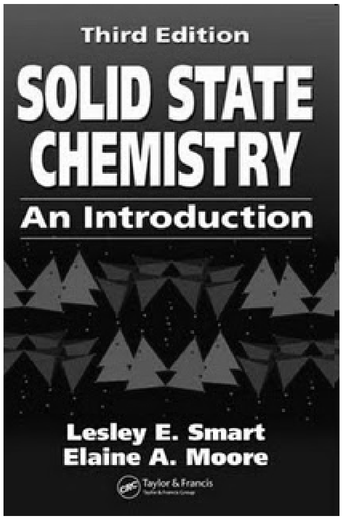




The Physics and Chemistry of Materials
Joel I. Gersten, Frederick W. Smith
ISBN: 978-0-471-05794-9 – Wiley

Inorganic Structural Chemistry - Second Edition
Ulrich Müller
ISBN: 978-0-470-01864-4 - Wiley





Basic Solid State Chemistry
Anthony R. West
ISBN: 978-0471987567 – Wiley

Solid State Chemistry
Lesley E. Smart, Elaine A. Moore
ISBN: 978-0748775163 - CRC Press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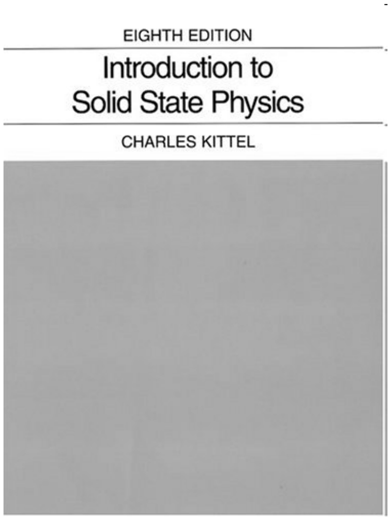
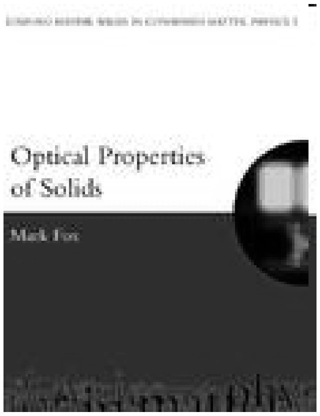
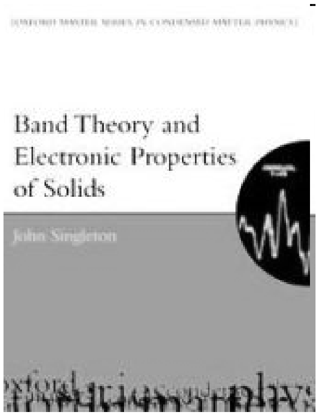
SOLID STATE PHYSICS


EIGHTH EDITION
Introduction to
Solid State Physics
CHARLES KITTEL

Solid State Physics
Neil W. Ashcroft, N. David Mermin
ISBN: 978-003083993 - Brooks Cole

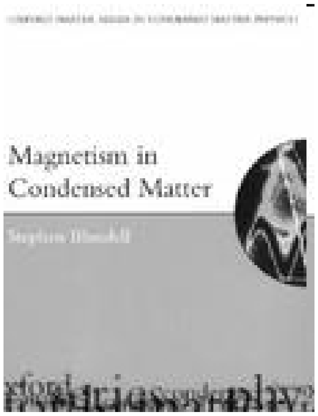
Introduction to Solid State Physics
Charles Kittel
ISBN: 978-0471415268 - Wiley


Optical Properties
of Solids
Mark Fox


Band Theory and
Electronic Properties
of Solids
John Singleton

Optical Properties of Solids
Mark Fox
ISBN: 978-0198506126 - Oxford University Press

Band Theory and Electronic Properties of Solids
John Singleton
ISBN: 978-0198506447 - Oxford University Press



Magnetism in Condensed Matter
Stephen Blundell
ISBN: 978-0198505914 - Oxford
University Press

The solid state is based on strong bonds:

Strong bonds: metallic, covalent and ionic

Weak Bonds: hydrogen, Van der Walls

Some of the physical properties of solid state materials are determined by three principal factors:

1 – The properties of the constituent atoms (masses, atomic numbers, electronic configurations, etc)

2 – The local interactions of atoms with each other in the solid state (i.e. the nature of the bonding and the resulting nearest-neighbor configurations of atoms)

3 – The arrangement of atoms in space to form a three dimensional solid

As a example, just by considering the nature of the bonding in solids its is possible to understand some of their basic macroscopic properties

⇒ Black board presentation
(Notes pages 1-3)

Structural Chemistry

For solid-state structures, there exists no systematic nomenclature which allows us to specify structural facts. One manages with the specification of *structure types* in the following manner: 'magnesium fluoride crystallizes in the rutile type', which expresses for MgF_2 a distribution of Mg and F atoms corresponding to that of Ti and O atoms in rutile.

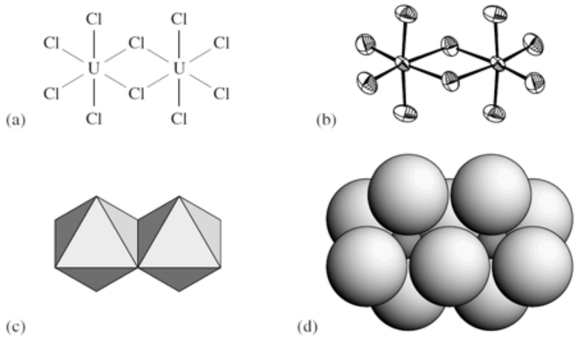


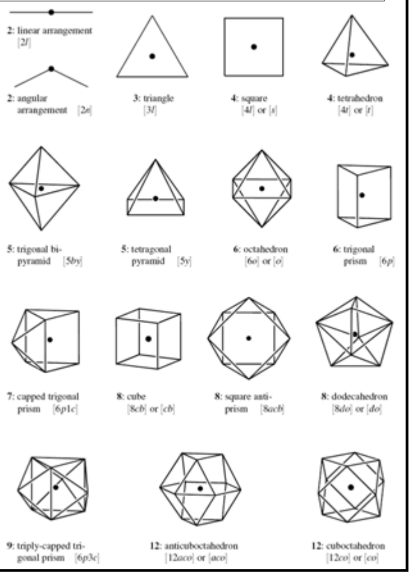
Fig. 2.1 Graphic representations for a molecule of $(UCl_5)_2$, all drawn to the same scale. **(a)** Valence-bond formula. **(b)** Perspective view with ellipsoids of thermal motion. **(c)** Coordination polyhedra. **(d)** Emphasis of the space requirements of the chlorine atoms

Quantitative specifications are made with numeric values for interatomic distances and angles. The interatomic distance is defined as the distance between the nuclei of two atoms in their mean positions (mean positions of the thermal vibration).

The coordination number (c.n.) and the coordination polyhedron serve to characterize the immediate surroundings of an atom. The *coordination number* specifies the number of coordinated atoms; these are the closest neighboring atoms

However, it is not always clear up to what limit a neighboring atom is to be counted as a closest neighbor

The *coordination polyhedron* results when the centers of mutually adjacent coordinated atoms are connected with one another. For every coordination number typical coordination polyhedra exist



Larger structural units can be described by connected polyhedra. Two polyhedra can be joined by a common vertex, a common edge, or a common face. The common atoms of two connected polyhedra are called bridging atoms. In face-sharing polyhedra the central atoms are closest to one another and in vertex-sharing polyhedra they are furthest apart

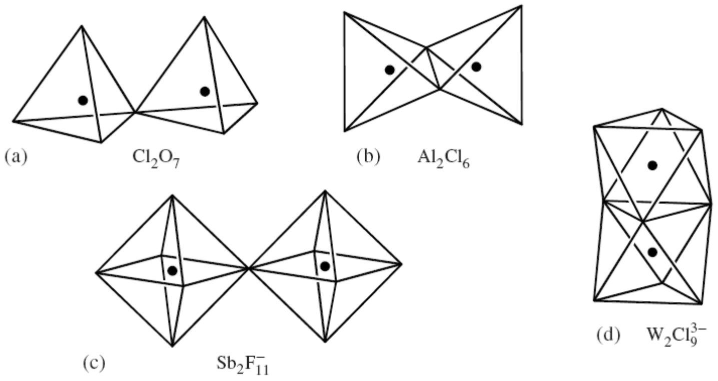


Fig. 2.3 Examples for the connection of polyhedra. (a) Two tetrahedra sharing a vertex. (b) Two tetrahedra sharing an edge. (c) Two octahedra sharing a vertex. (d) Two octahedra sharing a face. For two octahedra sharing an edge see Fig. 1

The Effective Size of Atoms

The electron density in an atom decreases asymptotically towards zero with increasing distance from the atomic center. An atom therefore has no definite size

When two atoms approach each other, interaction forces between them become more and more effective

Attractive are:

- The ever present dispersion force (LONDON attraction).
- Electronic interactions with the formation of bonding molecular orbitals (orbital energy) and the electrostatic attraction between the nuclei of atoms and electrons. These two contributions cause the bonding forces of covalent bonds.
- Electrostatic forces between the charges of ions or the partial charges of atoms having opposite signs.

Repulsive are:

- The electrostatic forces between ions or partially charged atoms having charges of the same sign.
- The electrostatic repulsion between the atomic nuclei.
- The mutual electrostatic repulsion of the electrons and the PAULI repulsion between electrons having the same spin. The PAULI repulsion contributes the principal part of the repulsion. It is based on the fact that two electrons having the same spin cannot share the same space. PAULI repulsion can only be explained by quantum mechanics, and it eludes simple model conceptions.

At some definite interatomic distance attractive and repulsive forces are balanced. This equilibrium distance corresponds to the minimum in a graph in which the potential energy is plotted as a function of the atomic distance

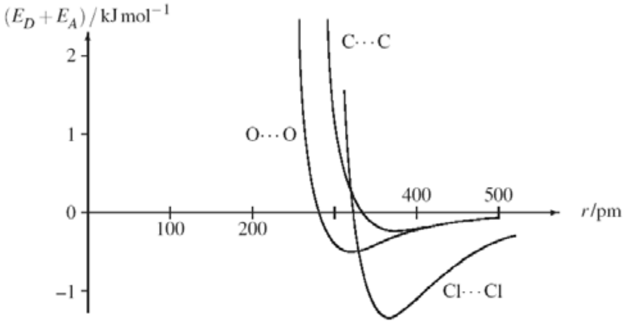


Fig. 5.1 Potential functions for the interaction energies due to repulsive and to dispersion forces between two atoms as a function of the interatomic distance

The equilibrium distance that always occurs between atoms conveys the impression of atoms being spheres of a definite size. In fact, in many cases atoms can be treated as if they were more or less hard spheres

Since the attractive forces between the atoms differ depending on the type of bonding forces, for every kind of atom several different sphere radii have to be assigned according to the bonding types. From experience we know that for one specific kind of bonding the atomic radius of an element has a fairly constant value

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We distinguish the following radius types: VAN DER WAALS radii, metallic radii, several ionic radii depending on the ionic charges, and covalent radii for single, double and triple bonds. Furthermore, the values vary depending on coordination numbers: the larger the coordination number, the bigger is the radius.

In a crystalline compound consisting of molecules, the molecules usually are packed as close as possible, but with atoms of neighboring molecules not coming closer than the sums of their VAN DER WAALS radii. The shortest commonly observed distance between atoms of the same element in adjacent molecules is taken to calculate the VAN DER WAALS radius for this element.

Table 6.1: Van der Waals radii /pm

H	120	spherical approximation [65, 67]						He	140
C	170	N	155	O	152	F	147	Ne	154
Si	210	P	180	S	180	Cl	175	Ar	188
Ge		As	185	Se	190	Br	185	Kr	202
Sn		Sb	200	Te	206	I	198	Xe	216

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Atomic radii in metals

The degree of cohesion of the atoms in metals is governed by the extent to which occupation of bonding electron states outweighs antibonding states in the electronic energy bands

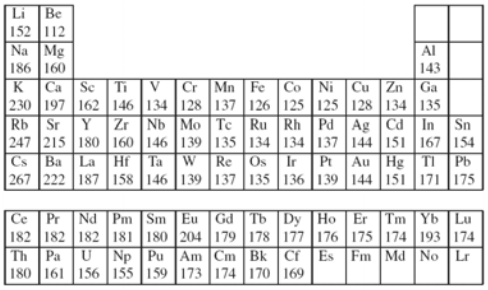
Metals belonging to groups in the left part of the periodic table have few valence electrons; the numbers of occupied bonding energy states are low.

Metals in the right part of the periodic table have many valence electrons; a fraction of them has to be accommodated in antibonding states. In both cases we have relatively weak metallic bonding

When many bonding but few antibonding states are occupied, the resulting bond forces between the metal atoms are large. This is valid for the metals belonging to the central part of the block of transition elements

Atomic radii in metals therefore decrease from the alkali metals up to the metals of the groups six to eight, and then they increase

Table 6.2: Atomic radii in metals/pm. All values refer to coordination number 12, except for the alkali metals (c.n. 8), Ga (c.n. 1+6), Sn (c.n. 4+2), Pa (c.n. 10), U, Np and Pu



Li 152	Be 112												
Na 186	Mg 160											Al 143	
K 230	Ca 197	Sc 162	Ti 146	V 134	Cr 128	Mn 137	Fe 126	Co 125	Ni 125	Cu 128	Zn 134	Ga 135	
Rb 247	Sr 215	Y 180	Zr 160	Nb 146	Mo 139	Tc 135	Ru 134	Rh 134	Pd 137	Ag 144	Cd 151	In 167	Sn 154
Cs 267	Ba 222	La 187	Hf 158	Ta 146	W 139	Re 137	Os 135	Ir 136	Pt 139	Au 144	Hg 151	Tl 171	Pb 175

Ce 182	Pr 182	Nd 182	Pm 181	Sm 180	Eu 204	Gd 179	Tb 178	Dy 177	Ho 176	Er 175	Tm 174	Yb 193	Lu 174
Th 180	Pa 161	U 156	Np 155	Pu 159	Am 173	Cm 174	Bk 170	Cf 169	Es	Fm	Md	No	Lr

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Covalent Radii

Covalent radii are derived from the observed distances between covalently bonded atoms of the same element

In the same way we calculate the covalent radii for chlorine (100 pm) from the Cl–Cl distance in a Cl_2 molecule, for oxygen (73 pm) from the O–O distance in H_2O_2 and for silicon (118 pm) from the bond length in elemental silicon

If we add the covalent radii for C and Cl, we obtain 77 + 100 =177 pm; this value corresponds rather well to the distances observed in C–Cl compounds

However, if we add the covalent radii for Si and O, 118 + 73 = 191 pm, the value obtained does not agree satisfactorily with the distances observed in SiO_2 (158 to 162 pm)

Generally we must state: the more polar a bond is, the more its length deviates to lower values compared with the sum of the covalent radii

Empirical corrections taking into account the polar character of the bond have been proposed

Ionic Radii

The shortest cation–anion distance in an ionic compound corresponds to the sum of the ionic radii. This distance can be determined experimentally. However, there is no straightforward way to obtain values for the radii themselves

The commonly used values for ionic radii are based on an arbitrarily assigned standard radius for a certain ion. In this way, a consistent set of radii for other ions can be derived

Ionic radii can also be used when considerable covalent bonding is involved. The higher the charge of a cation, the greater is its polarizing effect on a neighboring anion, i.e. the covalent character of the bond increases

The ionic radii listed in tables (cf. next slide) in most cases apply to ions which have coordination number 6. For other coordination numbers slightly different values have to be taken. For every unit by which the coordination number increases or decreases, the ionic radius increases or decreases by 1.5 to 2 %. For coordination number 4 the values are approximately 4 % smaller, and for coordination number 8 about 3 % greater than for coordination number 6. The reason for this is the mutual repulsion of the coordinated ions, the effect of which increases when more of them are present.

When covalent bonding is involved, the ionic radii depend to a larger extent on the coordination number. For instance, increasing the coordination number from 6 to 8 entails an increase of the ionic radii of lanthanoid ions of about 13 %, and for Ti^{4+} and Pb^{4+} of about 21 %. An ionic radius decrease of 20 to 35% is observed when the coordination number of a transition element decreases from 6 to 4

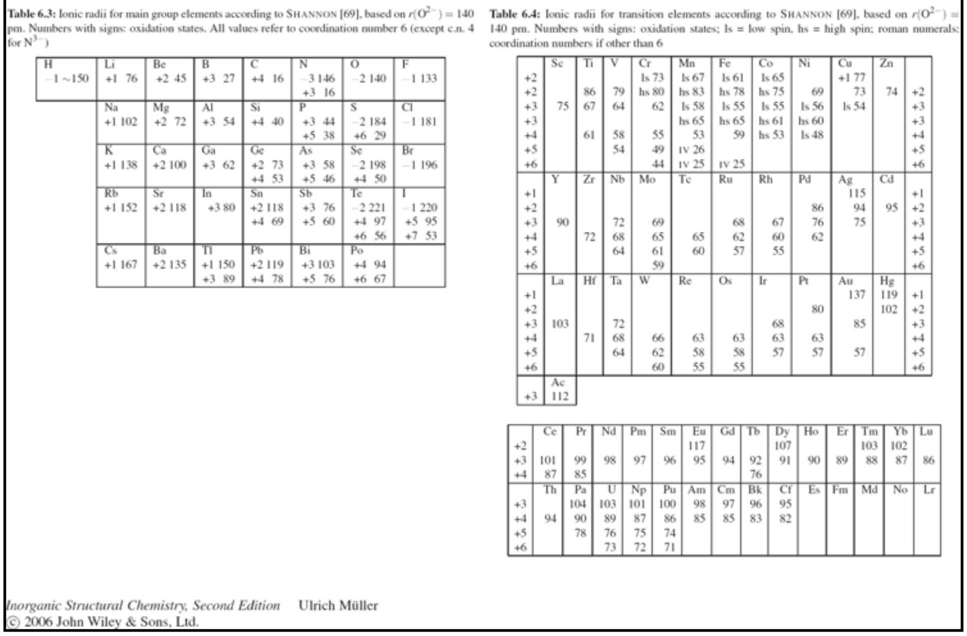

Table 6.3: Ionic radii for main group elements according to SHANNON [69], based on $r(O^{2-}) = 140$ pm. Numbers with signs: oxidation states. All values refer to coordination number 6 (except c.n. 4 for N^{3-})

H −1 ~150	Li +1 76	Be +2 45	B +3 27	C +4 16	N −3 146 +3 16	O −2 140	F −1 133
	Na +1 102	Mg +2 72	Al +3 54	Si +4 40	P +3 44 +5 38	S −2 184 +6 29	Cl −1 181
	K +1 138	Ca +2 100	Ga +3 62	Ge +2 73 +4 53	As +3 58 +5 46	Se −2 198 +4 50	Br −1 196
	Rb +1 152	Sr +2 118	In +3 80	Sn +2 118 +4 69	Sb +3 76 +5 60	Te −2 221 +4 97 +6 56	I −1 220 +5 95 +7 53
	Cs +1 167	Ba +2 135	Tl +1 150 +3 89	Pb +2 119 +4 78	Bi +3 103 +5 76	Po +4 94 +6 67	

Table 6.4: Ionic radii for transition elements according to SHANNON [69], based on $r(O^{2-}) =$ 140 pm. Numbers with signs: oxidation states; ls = low spin, hs = high spin; roman numerals: coordination numbers if other than 6

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
+2				ls 73	ls 67	ls 61	ls 65		+1 77		
+2		86	79	hs 80	hs 83	hs 78	hs 75	69	73	74	+2
+3	75	67	64	62	ls 58	ls 55	ls 55	ls 56	ls 54		+3
+3					hs 65	hs 65	hs 61	hs 60			+3
+4		61	58	55	53	59	hs 53	ls 48			+4
+5			54	49	IV 26						+5
+6				44	IV 25	IV 25					+6
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
+1									115		+1
+2								86	94	95	+2
+3	90		72	69		68	67	76	75		+3
+4		72	68	65	65	62	60	62			+4
+5			64	61	60	57	55				+5
+6				59							+6
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	
+1									137	119	+1
+2								80		102	+2
+3	103		72				68		85		+3
+4		71	68	66	63	63	63	63			+4
+5			64	62	58	58	57	57	57		+5
+6				60	55	55					+6
	Ac										
+3	112										

	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
+2						117			107			103	102	
+3	101	99	98	97	96	95	94	92	91	90	89	88	87	86
+4	87	85						76						
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
+3		104	103	101	100	98	97	96	95					
+4	94	90	89	87	86	85	85	83	82					
+5		78	76	75	74									
+6			73	72	71									

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