Acta Cryst. (1970). B**26**, 1044

Phases with Nowotny chimney-ladder structures considered as 'electron' phases.

By W. B. Pearson, *Department of Physics, University of Waterloo, Ontario, Canada*

(*Received* 18 *February* 1969 *and in revised form* 23 *December* 1969)

Phases with Nowotny chimney-ladder structures T_nX_m, where $2 > m/n \geq 1{\cdot}25$ have compositions m/n that are controlled in some way by electron concentration. The mechanism of structural stability is examined, particularly in relation to that of other 'electron' phases.

A new family of some 40 tetragonal structures of transition metal compounds, T_nX_m, where m and n are integers with $2 > m/n \geq 1{\cdot}25$ and X is a group III or IV metal, has been discovered largely by Nowotny and co-workers (Flieher, Völlenkle & Nowotny, 1968; Völlenkle, Preisinger, Nowotny & Wittmann, 1967; Völlenkle, Wittmann & Nowotny, 1966; see also Jeitschko & Parthé (1967) for earlier references) and reviewed by Jeitschko & Parthé (1967) and Parthé (1969). The unit cells of these structures all contain n pseudo-cells of a β-Sn like arrangement of T metal atoms stacked along the [001] direction, and m pseudo-cells of the X component stretched out to fill up the cell; hence the name chimney-ladder phases. The β-Sn like arrangement of T metal atoms arises from the T metals forming approximately equilateral triangular nets parallel to the (110) planes of the structures, which are stacked in the four possible positions $A'C'B'D'$, arising when the T node of one net lies not in the middle of the triangles of nets above and below, but over the opposite edges of the triangles, as in the $TiSi_2$ structure (Fig. 1). Since the unit cells of all of the structures contain four molecules, there are n β-Sn like cells stacked along **c**. It appears that m/n must have a value less than 2 in this family of tetragonal structures. When $m/n = 2$, the T and X atoms are coplanar and, with $A'C'B'D'$ stacking, this leads to orthorhombic symmetry in the $TiSi_2$ structure, and hexagonal symmetry and $A'B'C'$ stacking in the $CrSi_2$ structure, although the $MoSi_2$ structure with $A'B'$ stacking is tetragonal.

The importance of electron concentration in controlling the composition of the phases has been noted by Nowotny and co-workers and by Jeitschko & Parthé. The structures occur only at fixed compositions given by the m/n ratio and the value of n determines the size of the cell along **c**. I observe that the possible value(s) of m/n for any two components appear to be controlled by a unique relationship between the valency of the T atom, V_T, and the ratio mV_X/nV_T of the number of valence electrons contributed per formula by X to that contributed by T (counting outer s, p and d electrons) as shown in Fig. 2(*a*). Although the number of electrons per atom in the structures is uniquely prescribed according to the valency of the X and T atoms, there is no limiting value on its magnitude as indicated in Fig. 2(*b*). The electron concentration per T atom or per β-Sn pseudocell of T atoms is sensibly limited to 14 (or 56) as shown in Fig. 2(*c*), a fact also noted by Parthé. Indeed, the inflexion in the curve of Fig. 2(*a*), results from this limitation, since with the further limitation $m/n < 2$, it is not possible to maintain 14 electrons per T atom much below a V_T value of 7 (*i.e.* Mn) as indicated in Fig. 2(*c*). The unique curve of Fig. 2(*a*) at V_T values above 7 results from structural stability associated with 14 electrons per T atom, but why a unique curve still appears to control the compositions of structures at V_T values between 7 and 4 as the number of electrons per T metal atom in the structures decreases from 14 to 12, is not at present clear. Experience seems to show that any m/n ratio that gives a point lying sufficiently close to the line of Fig. 2(*a*), results in a new tetragonal structure of this general type, and structures containing as many as 600 atoms in the unit cell have been reported.

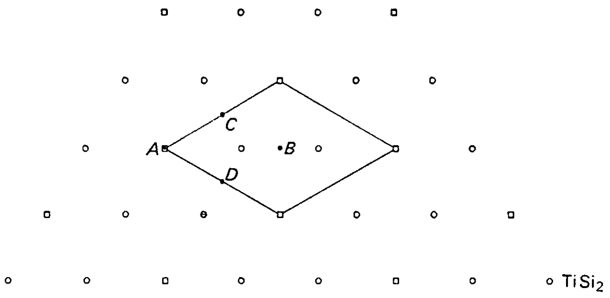

Fig. 1. Arrangement of atoms parallel to the (001) plane in the $TiSi_2$ structure, indicating a repeat cell and the four stacking positions $A'C'B'D'$.

These structures differ from others shown to depend on electron concentration, since structural control appears to result from a ratio, or the number of electrons *per single component*, rather than an overall number of electrons *per atom* in the structure. Furthermore, the near-neighbour coordination changes significantly from one structure to the next, which is not true of antiphase domain boundary changes of the first-kind, polytypic structural changes about the composition AB_3 (*e.g.* Sato & Toth, 1968) or polytypic Laves phase structure changes in certain ternary alloys (Komura, Kishida & Inoue, 1967; Komura, 1969; Laves & Witte, 1936) where structural control has been shown to result from overall electron concentration per atom. In these cases structural change essentially involves changes in second nearest neighbours. It has been demonstrated by Sato & Toth that this maintains planes of energy discontinuity about the Fermi surface in reciprocal space, lowering the overall electron energies and giving stability to different structural arrangements successively as the electron concentration is increased or decreased. The energy differences involved in these electronic changes and the associated changes in next nearest-neighbour coordination, make a much smaller contribution to the overall enthalpy, and therefore the free energy of such phases, than would changes in nearest-neighbour coordination. Hence, constancy of near-neighbour coordination appears to be a criterion for the observation of polytypic and similar structural changes which are controlled by electron concentration.

In the chimney-ladder structures the stretching of *m* pseudo-cells of X atoms to the height of *n* pseudo-cells of T atoms results in a 'sinusoidal' like variation of the T–X distances about T atoms on proceeding along [001], as noted by Völlenkle, Preisinger, Nowotny & Wittmann (1967) and shown in Fig. 3. The effect of this regularity may well be to give comparable average near-neighbour environments to the atoms in the different tetragonal structures, and thus comparable contributions to the enthalpy, so that there is little change on going from one structure to another, as regards the enthalpy contributions arising from near-neighbour interactions.

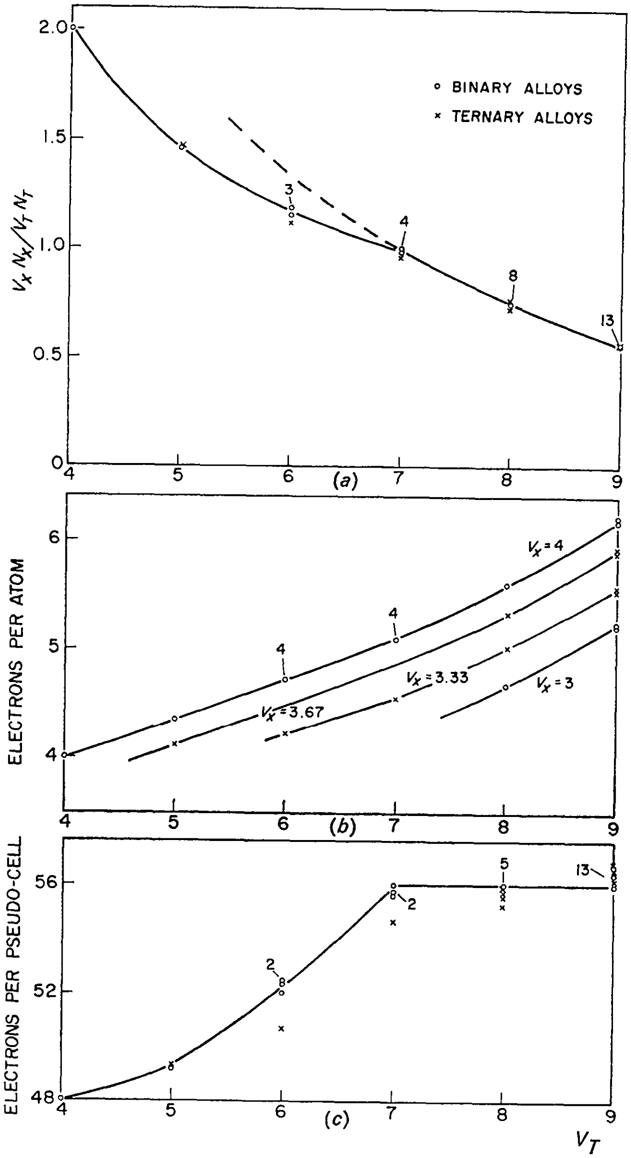

Fig. 2. Phases with Nowotny chimney-ladder structures: (*a*) the ratio mV_X/nV_T, (*b*) the number of electrons per atom, and (*c*) the number of electrons per β-Sn like T metal pseudo-cell, all as a function of the average number of electrons of the transition metal. ○ binary alloys, × ternary alloys. The numbers on the diagram indicate the number of different crystal structure types represented by a single point.

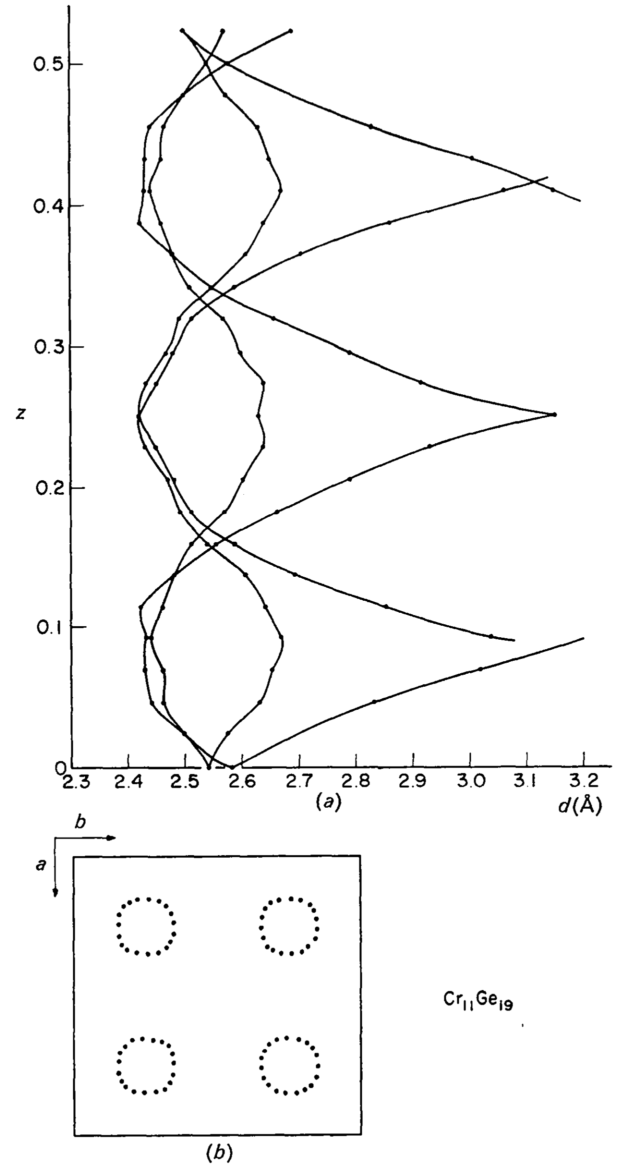

Fig. 3. (*a*) Cr–Ge interatomic distances in the $Cr_{11}Ge_{19}$ structure at fractional heights along [001] indicated by the ordinate, *z*. (*b*) Positions of the Ge atoms projected onto the (001) plane.

Since it can be demonstrated that the equilateral triangular arrangement of the T atoms in these structures controls the relative structural dimensions, and that there is no correlation between the relative dimensions of the β-Sn pseudo-cells and the composition ratio *m*/*n*, it cannot be argued that this pseudo-cell is anything more than a by-product of the *A'C'B'D'* stacking sequence of the T layers parallel to the (110) plane in the structures. Nevertheless, structural control by electron concentration of necessity involves some geometrical feature, since it results from the action of planes of energy discontinuity in reciprocal space. The one constant geometrical feature common to all of these 40 tetragonal structures is the β-Sn like pseudo-cell of T metal atoms with $c/na\sqrt{2}\simeq 0\cdot577=1/\sqrt{3}$ (the value for equilateral triangles in the nets of T atoms), so it would seem that structural stability must result from the achievement of some constant electron concentration within this psuedo-cell. This conclusion is entirely consistent with the observed fact that (at least for $V_T \geq 7$) the controlling feature is a constant electron concentration *per* T *atom* or per β-Sn like pseudo-cell, and not as in all other recognized cases of 'electron' phases, a controlling electron concentration *per atom* in the structure. Whether the 14 electrons per T atom represent 10 in inner filled energy bands and 4 in outer bands as in β-Sn itself, is an interesting speculation that magnetic measurements might solve.

References

FLIEHER, G., VÖLLENKLE, H. & NOWOTNY, H. (1968). *Mh. Chem.* **99**, 2408.

JEITSCHKO, W. & PARTHÉ, E. (1967). *Acta Cryst.* **22**, 417.

KOMURA, Y. (1969). Eighth International Congress of Crystallography, Stony Brook, N.Y., August.

KOMURA, Y., KISHIDA, E. & INOUE, M. (1967). *J. Phys. Soc. Japan*, **23**, 398.

LAVES, F. & WITTE, H. (1936). *Metallwirt.* **15**, 840.

PARTHÉ, E. (1969). In *Developments in the Structural Chemistry of Alloy Phases*, ed. GIESSEN, B. C., p. 49. New York: Plenum Press.

SATO, H. & TOTH, R. H. (1968). *Bull. Soc. Fr. Minér. Crist.* **91**, 557.

VÖLLENKLE, H., PREISINGER, A., NOWOTNY, H. & WITTMANN, A. (1967). *Z. Kristallogr.* **124**, 9.

VÖLLENKLE, H., WITTMANN, A. & NOWOTNY, H. (1966). *Mh. Chem.* **97**, 506,

---

Acta Cryst. (1970). B**26**, 1046

Revised values of effective ionic radii.*

By R. D. SHANNON and C. T. PREWITT,† *Central Research Department, E. I. du Pont de Nemours & Co., Experimental Station, Wilmington, Delaware* 19898, *U.S.A.*

(*Received* 12 *December* 1969)

Corrections resulting from an r^3 *vs.* a^3 replot of earlier data are presented for the ionic radii of rock salt, *C* rare earth, and fluorite oxides.

The non-equivalence of r^3 *vs.* a^3 and r *vs.* a plots for isotypic series of compounds was recently pointed out by Donnay (1969). We confirmed this non-equivalence empirically for the cubic series of rocksalt, *C* rare earth, and fluorite oxides by comparing both types of plot. Probably neither type is precisely linear. Thus, the choice of either r^3 *vs.* V or r *vs.* $V^{1/3}$ for derivation and comparison of ionic radii is arbitrary. Brisse & Knop (1968) used r *vs.* $V^{1/3}$ plots

Table 1(*a*). *Revised effective radii*†

EC, electron configuration; CN, coordination number; SP, electron spin; CR, crystal radii based on $r(^{VI}F^-)=1{\cdot}19$ Å; 'IR', effective ionic radii based on $r(^{VI}O^{2-})=1{\cdot}40$ Å. Values of radii taken from radii *vs.* volume plots are marked by *R*, doubtful values by ? and values for which at least 5 structural determinations resulted in radii differing by no more than $\pm 0{\cdot}01$ Å are marked with an asterisk.

Ion	EC	CN	SP	Shannon & Prewitt (1969) CR	'IR'
Am^{3+}	$5f^6$	VI		1·14	1·00 *R*
Br^{7+}	$3d^{10}$	IV		0·40	0·26
Cd^{2+}	$4d^{10}$	IV		0·94	0·80
Ce^{3+}	$6s^1$	VI		1·15	1·01 *R*
		IX		1·29	1·15
Co^{2+}	$3d^7$	IV	HS	0·71	0·57
		VI	HS	0·885	0·745*R**
Cs^{1+}	$5p^6$	VIII		1·96	1·82 ?
D^{1+}	$1s^0$	II		0·04	−0·10 ?
Dy^{3+}	$4f^9$	VI		1·052	0·912*R*
Er^{3+}	$4f^{11}$	VI		1·030	0·890*R*
Eu^{3+}	$4f^6$	VI		1·087	0·947*R*
		VII		1·17	1·03
Fe^{2+}	$3d^6$	VI	HS	0·920	0·780*R**
Gd^{3+}	$4f^7$	VII		1·18	1·04
Ho^{3+}	$4f^{10}$	VI		1·041	0·901*R*
In^{3+}	$4d^{10}$	VI		0·940	0·800*R**
La^{3+}	$4d^{10}$	VI		1·185	1·045*R*
Lu^{3+}	$4f^{14}$	VI		1·001	0·861*R*
Mg^{2+}	$2p^6$	IV		0·72	0·58
		V		0·81	0·67
Mn^{2+}	$3d^5$	VI	HS	0·970	0·830*R**
Mn^{3+}	$3d^4$	VI	HS	0·785	0·645*R**
Nd^{3+}	$4f^3$	VI		1·123	0·983*R*

---

*Contribution No. 1646.

†Present address: Dept. of Earth and Space Sciences, State University of New York, Stony Brook, L. I., New York 11790, U.S.A.