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# The oxidation resistance and constitution of compounds of groups IIIA and IVA with d-transition elements

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The thermal oxidation resistance of intermetallic compounds from the following groups of alloys has been tested by an isochronal method: (a) yttrium, lanthanum, cerium, gadolinium, titanium and zirconium separately with the series of elements chromium to gallium, (b) titanium with the elements palladium, silver, cadmium, platinum and gold and (c) some miscellaneous compounds marginal to (a) and (b). The ratio of the oxidation parameter to the decomposition point ($T_p/T_m$) has been plotted on appropriate synoptic diagrams, from which it is evident that maxima in $T_p/T_m$ occur at Ni (group III)$_3$ or Ni (group IV)$_2$. Extensions of high $T_p/T_m$ stretch in two directions in the diagrams from the maxima, namely $NiR_3 \rightarrow Fe_2R$ and $NiR_3 \rightarrow CuR$, from which it is inferred that these maxima and extensions, which are indicative of a considerable degree of chemical binding, are related to bonding across the transition metal and composite divides respectively. Substitution of palladium or platinum for nickel, or of zirconium for titanium, results in diminution in $T_p/T_m$, and this is thought to be due to the operation of a supplementary valency effect.

## 1. Introduction

If we consider the thermal oxidation resistance of inorganic compounds in their entirety we find, broadly speaking, that they may be divided into two classes characterized by adherence to either a $T_p/T_m \sim 0.5$ or $T_p/T_m \sim 1.0$ regime, where $T_p$ is an empirical temperature representing the onset of terminal oxidation, and $T_m$ is the compound melting point on the Kelvin scale. Furthermore, families of compounds of the 1.0 regime have been found where the components come from well defined areas of the periodic table, that is, when the components straddle what the author has termed the divides in the periodic table (Fig. 1). Typical of such behaviour are GaAs (formed across the covalent divide), and beta and gamma brass (across the composite divide); it would seem likely that compounds across the ionic divide are also of the same nature.

Thus far, a high degree of consistency is apparent in the incidence *vis a vis* the periodic table, a consistency which finds parallels in the types of phase diagram in the appropriate systems. Simply from the nature of the phase diagrams, it had become apparent that a divide must be drawn in the middle of the transition series. However, earlier oxidation studies of some inter-transition metal compounds [1] showed that they obeyed a 0.5 $T_m$ regime in the standardized test. This was a disappointment, but in a vague way one invoked electron delocalization for the absence of 1.0 $T_m$ behaviour. The situation changed when it was found [2] that $Y_9Co_7$ and some other compounds in the Y–Co system showed ratios significally above 0.5, and by replacing components in turn on the yttrium or cobalt sites, other similar phases were discovered. A hypothesis was advanced in respect of the high ratios (i.e. the high effect), but further inference was made difficult by the absence of sufficiently comprehensive data relative to selected fixed components. The work was therefore re-orientated and expanded on the following lines.

Since the early work had tested compounds whose components come from near the transition metal divide (e.g. $TiMn_2$, VFe) attention was moved to instances where components come from the flank of the same series. The concomitant assumption was made that high effect was more likely to be found amongst line compounds. This effectively means elements of groups IIIA and IVA (the former including all the lanthanide metals) as the first-named component, since groups VA and VIA are pre-eminently formers of variable stoichiometry phases such as sigma, and only a few compounds of calcium, strontium and barium with transition elements are known (e.g. $CaCu_5$). A complete study of these elements in turn with respect to all the d-transition elements would indeed be a formidable undertaking, and the present paper is largely concerned with the selection yttrium, lanthanum, cerium, gadolinium, titanium or zirconium as early group components and, for the most part, the first long period elements as the other component.

As the work progressed, results were collated by the use of synoptic diagrams, several of which are reproduced herein. In these, the positions of compounds

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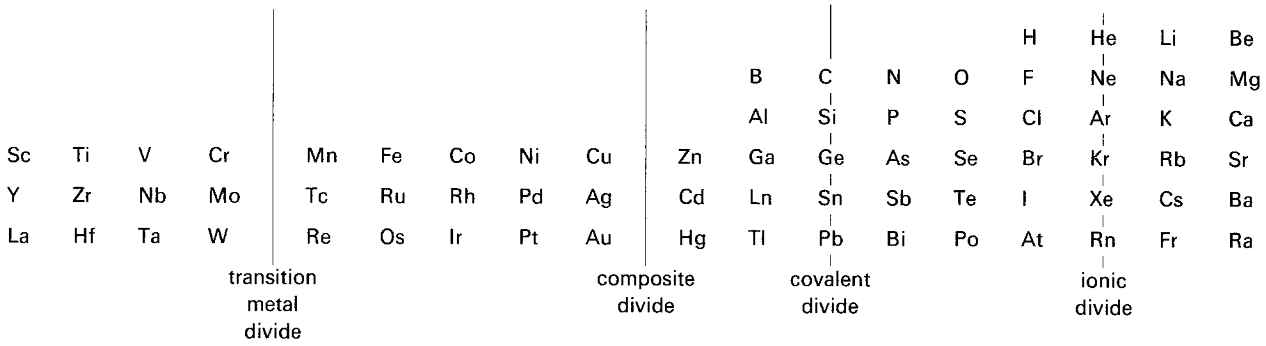

*Figure 1* The periodic table with divides added.

are marked at their appropriate positions on tie lines, each of which represents a binary system. The lines can be likened to rungs on ladders, complete ladders having uprights which represent a series of elements and a constant element respectively. A diagram is first constructed so as to show the incidence of known compounds [3, 4]. Subsequently, values for $T_p/T_m$ which are already known from either the paper immediately preceding [2] or from early work [1] were marked in, and decisions made as to new compositions of probable high effect. In other words, the work became tactically a typical hill-finding exercise, with $T_p/T_m$ as the counterpart of the height variable. The heights and gradients involved are modest in comparison with the earlier studies across the composite divide (e.g. [5]).

## 2. Experimental details

Single samples weighing approximately 1 g and of surface area about 1 $\text{cm}^2$ were prepared by direct synthesis from Johnson Matthey "Specpure/Puratronic" (5N) and Rare Earth Products (3N, except Y 4N) metals. Alloys containing zinc or cadmium were melted in evacuated fused quartz capsules for $\frac{1}{4}$h at 1000° C followed by air cooling. The remaining alloys were prepared in an argon-arc furnace, aiming for the melting current sequence of 60–80–100–125–125 A established previously [2]. Many of the melted buttons were suction cast into a 2.3 mm diameter copper mould; this produced some increase in surface area relative to a button shape, and allowed for more accurate mensuration. Weight losses were of the order of 0.2%. The weight of alloys $R_3T$, where R is lanthanium or cerium and T is a d-transition metal, was monitored for some hours after first exposure to air, to confirm stability at room temperature. Samples were white, except for copper-rich compositions; $CeCu_2$ looked like brass. Tests at this stage showed that the following were attracted to a pocket magnet: $YMn_2$, $YFe_2$, $YCo_5$, $Y_9Co_7$, $LaCo_2$ (slightly), $Gd_6Mn_{23}$, $GdFe_2$, $GdCo_2$, GdCo and $DyCo_2$.

Oxidation testing consisted of heating in air to successively higher temperatures (200, 400, then at 100° C intervals) for a fixed time of 4 h at each temperature, until the temperature ($T_p$) corresponding to a weight change of 1 $\text{mg cm}^{-2}$ over the 4 h could be interpolated. In most cases a weight gain was registered, but the following were exceptions: $CaCu_6$, TiZn, TiCd, $CeCu_6$, $GdMn_2$, $DyCo_2$ and $ErCo_2$. The $T_p$ results for $Gd_3Co$, GdNi, $DyCo_2$ and $Dy_3Co$ were

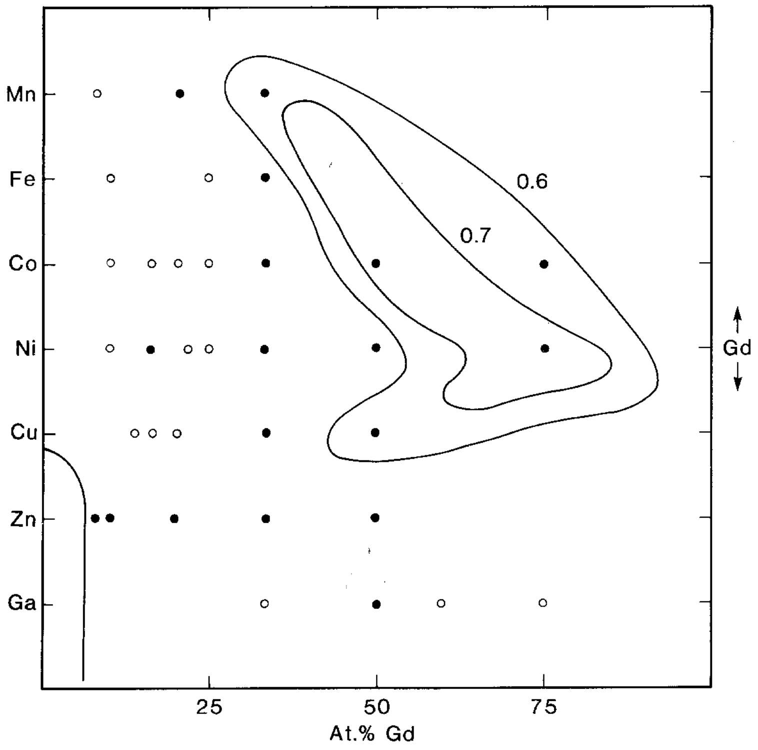

*Figure 2* Synoptic diagram for compounds of gadolinium with elements of the first long period.

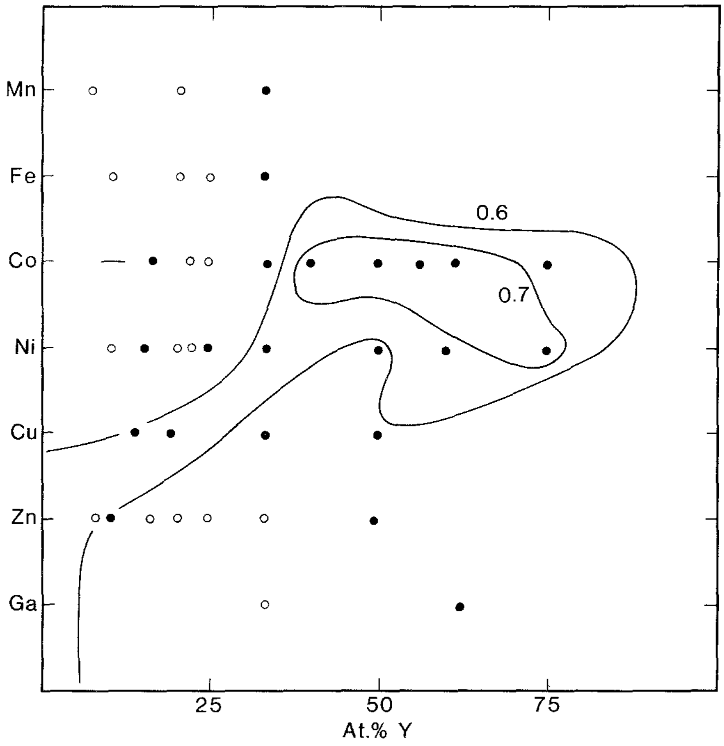

*Figure 3* As Fig. 2 for yttrium compounds.

extrapolated. A tendency to a "chromium" type of $T/w$ curve (where a significant degree of weight uptake is found at temperatures much lower than turnover) was noted for $TiCu_3$, $TiPt_3$, $Zr_2Ni$ and ZrAg.

## 3. Results

The complete results are presented in Tables I to VIII, but the significant features will be apparent from the synoptic diagrams Figs 2 to 6 inclusive. In these the compositions of compounds are marked by open circles (lines where composition range is large), and tested compositions by closed circles. The data from the tables are utilized to superimpose contour lines for $T_p/T_m = 0.6$ and 0.7 to indicate the zones of high effect. Thus each diagram gives information of two interrelated but different types, namely, the incidence of compounds and the incidence of effect. The pattern of incidence of compounds does not change in type whichever group IIIA or IVA element be taken as the common component, and this part of the experimental picture is easily described. The envelope of distribution is a line starting from the transition-metal (i.e. left-hand) ordinate about half-way along the d-series which moves toward the constant element ordinate with increasing group number. After encompassing compounds of type $R_3Co$ and $R_3Ni$, the envelope tends to the point representing RZn, since high R/Zn compounds do not exist. Within the envelope, many of the compounds fall on parallel lines of constant atomic ratio.

The locations of the zones of high effect are more variable, but general tendencies are evident. The latter are of two types, one for high effect to occur along a

TABLE I Summary of oxidation tests on gadolinium compounds c congruent formation, p peritectic, pd peritectoidal

| Composition | $T_p$ (°C) | $T_m$ | $T_p/T_m$ |
|---|---|---|---|
| $Gd_6Mn_{23}$ | 420 | 1050p | 0.52 |
| $GdMn_2$ | 570 | 950p | 0.69 |
| $GdFe_2$ | 400 | 1150p | 0.47 |
| $GdCo_2$ | 360 | 1100p | 0.47 |
| GdCo | 580 | 880p | 0.74 |
| $Gd_3Co$ | 400 | 780p | 0.64 |
| $GdNi_5$ | 390 | 1500c | 0.37 |
| $GdNi_2$ | 440 | 1070p | 0.53 |
| GdNi | 420 | 980c | 0.55 |
| $Gd_3Ni$ | 570 | 775p | 0.80 |
| $GdCu_2$ | 440 | (1050) | (0.54) |
| GdCu | 450 | (800) | (0.67) |
| $GdZn_{11}$ | 460 | (1200) | (0.50) |
| $Gd_2Zn_{17}$ | 420 | (1300) | (0.44) |
| $GdZn_4$ | 340 | (1300) | (0.39) |
| $GdZn_2$ | 350 | (1050) | (0.47) |
| GdZn | 190 | (800) | (0.43) |
| GdGa | 330 | | |
| GdGe | 320 | | |

TABLE II As Table I for yttrium compounds

| Composition | $T_p$ (°C) | $T_m$ | $T_p/T_m$ |
|---|---|---|---|
| $YMn_2$ | 460 | 1102c | 0.53 |
| $YFe_2$ | 470 | 1125p | 0.53 |
| $YCo_5$ | 450 | 1352p | 0.44 |
| $YCo_2$ | 380 | 1150p | 0.46 |
| $Y_2Co_3$ | 590 | 860p | 0.76 |
| YCo | 540 | 802p | 0.76 |
| $Y_9Co_7$ | 610 | 725pd | 0.88 |
| $Y_8Co_5$ | 570 | 740p | 0.83 |
| $Y_3Co$ | 480 | 880p | 0.65 |
| $YNi_5$ | 490 | 1490c | 0.43 |
| $YNi_3$ | 420 | 1237p | 0.46 |
| $YNi_2$ | 590 | 1115p | 0.62 |
| YNi | 500 | 1045c | 0.59 |
| $Y_3Ni_2$ | 470 | 835p | 0.67 |
| $Y_3Ni$ | 580 | 898p | 0.73 |
| $YCu_6$ | 450 | 930p | 0.60 |
| $YCu_4$ | 510 | 965c | 0.63 |
| $YCu_2$ | 430 | 935c | 0.58 |
| YCu | 440 | 935c | 0.59 |
| $Y_2Zn_{17}$ | 400 | 895c | 0.58 |
| YZn | 330 | 1095c | 0.44 |
| $Y_5Ga_3$ | 350 | | |

TABLE III As Table I for cerium compounds

| Composition | $T_p$ (° C) | $T_m$ | $T_p/T_m$ |
|---|---|---|---|
| $CeFe_2$ | 130 | 925p | 0.34 |
| $CeCo_2$ | 170 | 1035p | 0.34 |
| CeCo | 170 | (670) | (0.47) |
| $Ce_3Co$ | 170 | 480c | 0.59 |
| $CeNi_4$ | 340 | 1065p | 0.46 |
| $CeNi_3$ | 240 | 930p | 0.43 |
| $CeNi_2$ | 190 | 830p | 0.42 |
| CeNi | 110 | 670c | 0.41 |
| $Ce_3Ni$ | 290 | 485c | 0.74 |
| $CeCu_6$ | 340 | 940c | 0.51 |
| $CeCu_4$ | 410 | 780p | 0.65 |
| $CeCu_2$ | 160 | 820c | 0.40 |
| CeCu | 250 | 515p | 0.66 |
| $Ce_3Cu$ | 200 | (485) | (0.62) |
| $CeZn_4$ | 310 | (870) | (0.51) |
| $CeZn_2$ | 170 | 875c | 0.39 |
| CeZn | 160 | 825c | 0.39 |

TABLE V As Table I for titanium-3d compounds

| Composition | $T_p$ (° C) | $T_m$ | $T_p/T_m$ |
|---|---|---|---|
| $TiCr_2$ | 740 | 1350 | 0.62 |
| $TiMn_2$ | 550 | 1325p | 0.52 |
| TiMn | 680 | 1175p | 0.66 |
| $TiFe_2$ | 660 | 1427c | 0.55 |
| TiFe | 680 | 1317 | 0.60 |
| $Ti_2Fe$ | 700 | 1200 | 0.66 |
| $Ti_2Co_7$ | 790 | 1080pd | 0.79 |
| $TiCo_2$ | 750 | 1250p | 0.67 |
| TiCo | 780 | 1300c | 0.67 |
| $Ti_2Co$ | 770 | 1250p | 0.68 |
| $TiNi_3$ | 730 | 1376c | 0.61 |
| TiNi | 740 | 1240c | 0.67 |
| $Ti_2Ni$ | 690 | 1015 | 0.75 |
| $TiCu_3$ | 660 | 895p | 0.81 |
| $TiCu_2$ | 640 | 855p | 0.81 |
| $Ti_2Cu_3$ | 710 | 955p | 0.80 |
| TiCu | 670 | 980c | 0.75 |
| $Ti_2Cu$ | 850 | 990p | 0.89 |
| $TiZn_{15}$ | 560 | 445p | 1.16 |
| $TiZn_5$ | 520 | 650p | 0.86 |
| $TiZn_3$ | 520 | 920c | 0.66 |
| $TiZn_2$ | 570 | 930p | 0.70 |
| TiZn | 400 | 1070p | 0.50 |
| $TiGa_3$ | 340 | 925p | 0.51 |
| $TiGa_2$ | 400 | 1170c | 0.47 |

line approximately $R_3Ni$–$RFe_2$, and secondly along a line $R_3Ni$–RCu. For brevity we call these the TM and CD trends respectively. Particularities differ from one R (group IIIA/IVA) element to another, and may be described as follows. In Fig. 2 the 0.6 *and* 0.7 contour lines delineate an area which trends towards the TM ordinate with decreasing group number, though not reaching it. A CD trend also exists which again stops short of that ordinate. For yttrium (Fig. 3) there is a strong TM trend in the direction of RCo and a weaker CD trend which reaches CuZn. The tail of the latter extending downwards to gallium is an acknowledgement of the fact that the *elements* zinc, gallium and germanium show high effect [6]. Fig. 4 (Ce) shows high effect at $Ce_3Ni$ from which a weak CD trend develops. For lanthanum (Fig. 5) characterization of the trends along the lines adopted is more difficult, although there is no mistaking the strong 0.6 and 0.7 presence at the intersection of our archetypal TM and CD lines. Titanium (Fig. 6) shows a strong CD trend, a weak TM trend, and an outlying high point at $Ti_2Co_7$. If we plot the data (Table VI) for titanium-second long period (this and the titanium-third long period counterpart are not illustrated) we will find a zone of quite high effect around $Ti_2Pd$ and $Ti_2Ag$, but the limited data do not permit us to infer extensions from this zone. However, from Ti–Pt and Ti–Au it is clear that no high effect zone of any consequence occurs in the titanium-third long period. Finally, if we revert to 3d elements on the left-hand ordinate, but make the common group IV element zirconium rather than titanium (Table VII), we find graphical evidence somewhat like that for cerium-first long period (Fig. 4). For elements on the route in the periodic table Zr–Ti–Cu–Au, in short, any substitution with components from higher number periods results in diminution of effect.

## 4. Discussion

For reasons which will become apparent, we commence with a consideration of some general chemistry. We know that elements near to but on opposite sides of the ionic divide (Fig. 1) react together to form alkali and alkali-earth halides and of predominantly ionic character. When, however, chlorine, for example is reacted with aluminium, a trivalent element, the resultant degree of ionicity is markedly less, and with silicon, still further from that divide, we arrive at compounds of essentially covalent character. At this divide the average group number of compounds will be zero, using an ionic group number count in which

TABLE IV As Table I for lanthanum compounds

| Composition | $T_p$ (° C) | $T_m$ | $T_p/T_m$ |
|---|---|---|---|
| $LaCo_2$ | 290 | (827) | (0.51) |
| LaCo | 440 | (685) | (0.74) |
| $La_3Co$ | 370 | (515) | (0.82) |
| $LaNi_2$ | 340 | 827p | 0.56 |
| LaNi | 390 | 685c | 0.69 |
| $La_3Ni$ | 320 | 515c | 0.75 |
| $LaCu_2$ | 300 | 834c | 0.52 |
| LaCu | 390 | 551p | 0.80 |
| $La_3Cu$ | 410 | (515) | (0.87) |
| $LaZn_2$ | 200 | 855c | 0.42 |
| LaZn | 170 | 815c | 0.41 |
| $La_3Zn$ | 190 | (515) | (0.59) |

TABLE VI As Table I for titanium-4d and 5d compounds

| Composition | $T_p$ (° C) | $T_m$ | $T_p/T_m$ |
|---|---|---|---|
| $TiPd_3$ | 800 | 1720c | 0.54 |
| TiPd | 800 | (1200) | (0.73) |
| $Ti_2Pd$ | 820 | 1150pd | 0.77 |
| TiAg | 500 | 1030p | 0.59 |
| $Ti_3Ag$ | 760 | 930p | 0.86 |
| TiCd | 360 | (1070) | (0.47) |
| $TiPt_3$ | 1160 | 1950c | 0.64 |
| TiPt | 690 | 1830c | 0.46 |
| $Ti_3Pt$ | 740 | 1370c | 0.62 |
| $TiAu_2$ | 460 | 1455c | 0.42 |
| TiAu | 530 | 1490c | 0.46 |
| $Ti_3Au$ | 790 | 1395c | 0.64 |

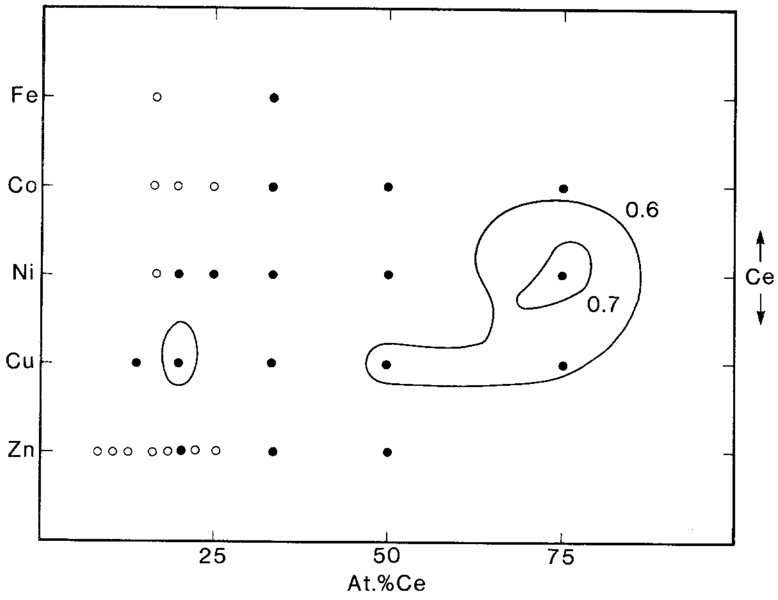

*Figure 4* As Fig. 2 for cerium compounds.

chlorine equals minus 1, not plus 7. If we now express these generalities in the formalism favoured by the author, we can draw a double hyperbola on a duplex synoptic diagram (Fig. 7) using such group number/valency values. The compounds formed by potassium (KCl, $K_2S$ etc) and chlorine (KCl, $CaCl_2$) may be expressed by points falling on one line (AA). If for the matched pair of common elements we chose calcium and sulphur instead of potassium and chlorine, the formalism gives us a hyperbola with a more gentle curve (BB), and so on with CC etc. Lines of compound points parallel to ordinates will be produced where components have equal valencies, or by a row of elements on an ordinate having constant valencies as can happen with the 3d elements [7]. Compound points not on the hyperbola of normal valency may in other instances be connected with the incidence of bonding variations (e.g. double bonds). Examples of non-hyperbola compounds are the oxides of sodium other than $Na_2O$, and the lower fluorides of sulphur; covalencies are involved, and it will be noted that the points occur *inside* the hyperbola. When we apply this approach to the composite divide (Fig. 1), much of the argument can be transferred, but there is a difference in the atomic structures, that is, we must "add on" the s electrons, representing the outer stratum.

One consequence of this modification is that the divide occurs between groups IB and IIB (i.e. between elements of AGN (average group number) 1 and 2) instead of through nickel, palladium and platinum (AGN zero, counting down from zinc 2, copper 1). The situation at the transition metal divide bears a general resemblance to that at the composite divide, so, *mutatis mutandis*, the divide lies between groups VIA and VIIA instead of through vanadium, niobium and tantalum (the latter representing a primitive full half d shell with no s electron layer). For components such as chromium plus manganese, or copper plus zinc, families of typical compounds such as sigma and gamma brass lie on or near hyperbolae in the synoptic diagrams. With common components further from the divide, compounds on hyperbolae give way to an incidence pattern, as noted above for the ionic divide, of compound points inside hyperbolae. However, here the non-hyperbola points are altogether more numerous, although an envelope which can well be envisaged as a hyperbola is retained.

The second consequence of the modification is that the chemical combination of the peripheral and core electrons present in sigma and gamma phases loosens gradually and becomes the process of s–d resonance, in which an s electron on one site combines momentarily into an adjoining d shell, followed by activation

TABLE VII As Table I for zirconium compounds

| Composition | $T_p$ (°C) | $T_m$ | $T_p/T_m$ |
|---|---|---|---|
| $ZrCr_2$ | 500 | 1675c | 0.40 |
| $ZrFe_2$ | 480 | 1645c | 0.39 |
| ZrCo | 590 | 1360c | 0.53 |
| $Zr_2Co$ | 370 | 1130c | 0.46 |
| ZrNi | 480 | 1470c | 0.43 |
| $Zr_2Ni$ | 740 | 1200c | 0.69 |
| $ZrCu_3$ | 440 | 1115c | 0.51 |
| $Zr_2Cu_3$ | 480 | 895c | 0.64 |
| ZrCu | 490 | 940c | 0.63 |
| $Zr_2Cu$ | 530 | 1000c | 0.63 |
| $ZrZn_2$ | 340 | 1180c | 0.42 |
| ZrZn | 340 | 1110p | 0.44 |

TABLE VIII As Table I for miscellaneous compounds

| Composition | $T_p$ (°C) | $T_m$ | $T_p/T_m$ |
|---|---|---|---|
| $CaCu_6$ | 180 | 935c | 0.38 |
| $BaCu_{13}$ | 360 | 675p | 0.67 |
| $Y_3Si_5$ | 490 | 1635 | 0.40 |
| $Y_5Si_3$ | 530 | 1850c | 0.38 |
| $CeAg_3$ | 170 | 990c | 0.35 |
| CeAg | 190 | 855c | 0.41 |
| $DyCo_2$ | 240 | 1300p | 0.33 |
| $Dy_3Co$ | 440 | 794p | 0.67 |
| $ErCo_2$ | 190 | 1500 | 0.26 |
| $Er_3Co$ | 370 | 900p | 0.55 |
| ZrAg | 450 | 1135 | 0.51 |
| $Zr_2Ag$ | 260 | 1391p | 0.32 |
| HfCo | 690 | 1480c | 0.55 |
| $Hf_2Co$ | 650 | 1480c | 0.53 |
| $V_3Co$ | 570 | 1125p | 0.60 |
| $V_3Ge$ | 580 | (1525p) | 0.47 |
| $TaCo_2$ | 670 | 1593p | 0.51 |

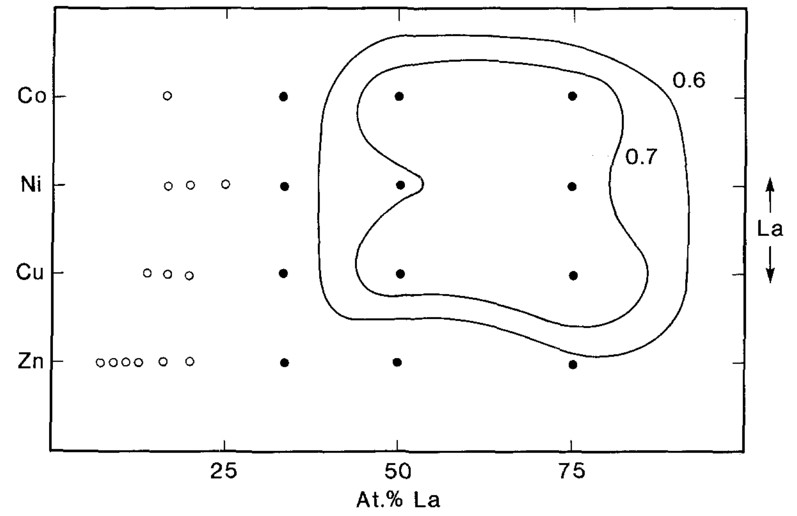

*Figure 5* As Fig. 2 for lanthanum compounds.

to s state and so on. The loosening is to a degree already present in gamma and sigma, as shown by the stoichiometry range in these phases; it is essentially complete in solid solutions between such elements as nickel and cobalt. It is this resonance which is responsible for the 0.5 $T_m$ relation, and for specifically metallic properties.

We can now understand in principle the reasons for our patterns of compound incidence if we turn to the schematic Fig. 8. In order to maintain the link in discussion with the argument from the whole of the periodic table, this diagram runs to the end of the long period. The line AB at the bottom represents an ionic divide hyperbola which intersects the left-hand ordinate at the noble gas; this is also an envelope. Line CDEF is the envelope for the compounds of this paper, as already mentioned. We superimpose in explanation of our results two hyperbolae. Curve xy is a composite divide hyperbola which as realised in the figure cuts the transition metal ordinate between copper and zinc, and yz a transition metal divide hyperbola cutting between manganese and chromium. Curves xy and yz are for AGN 1.5 to simplify drawing, but fundamentally will be golden ratio-related. The ionic hyperbola codifies what are commonly agreed to be normal valency compounds, xy the main trends of our cerium, titanium and zirconium compounds (Figs 4 and 6, and Table VII), and yz the main trends of the gadolinium and yttrium compounds (Figs 2 and 3). Taking a wide sweep over our corpus of data, we note the bracketing of cerium with titanium/zirconium, the CD trend with titanium (Fig. 6) where the 0.6 actually reaches the left-hand ordinate near zinc, and the fact that the 0.6 for titanium, yttrium, lanthanum and gadolinium stop short of that ordinate at the top-left in Figs 2–6, which are consistent respectively with tetravalency in cerium, titanium in a zinc pseudo-position in the periodic

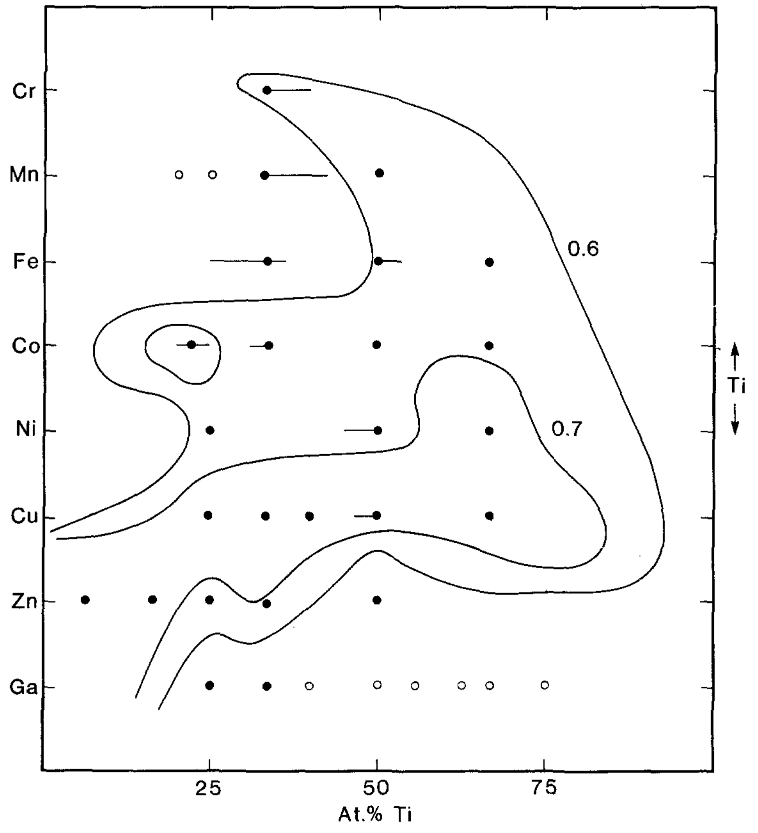

*Figure 6* As. Fig. 2 for titanium compounds.

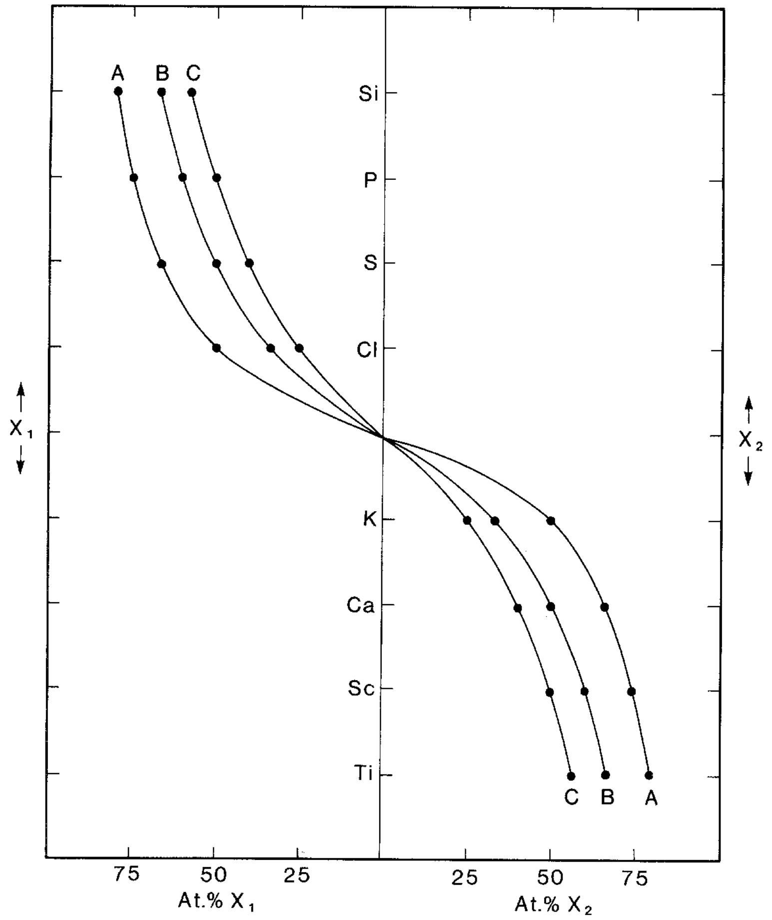

*Figure 7* Systematics of compound incidence across the ionic divide. For hyperbolae AA, $X_1$ = K and $X_2$ = Cl, for hyperbolae BB, $X_1$ = Ca and $X_2$ = S, for hyperbolae CC, $X_1$ = Sc and $X_2$ = P.

table, and the distance of yttrium, titanium, lanthanum and gadolinium from the transition metal divide. Note also the ranges of stoichiometry for titanium Laves phases (Fig. 6), consistent with a second-order (s–d resonance) contribution to bonding, which explains the occurrence of $TiCo_2$ but no $TiNi_2$ [8] but, more importantly for this paper, illustrates just what we would expect from the theoretical argument, that the degree of s–d resonance will, other things being equal, be greater towards the left-hand (TM) axis.

It is at this point that we are faced with a conflict of interpretation. Do we assert that, normally, compounds of transition metals show low effect, but that the presence of some elements (e.g. yttrium, copper) flanking the central transition metals in the periodic table imposes high effect, or, alternatively, is high effect normality and low due to a short-circuiting superposition of s–d resonance? The former suggests lapping up of residual bonding, possible only in the vicinity of hyperbolae, whilst the latter hypothesis falls more naturally into an overall schema of combinatory interactions, in which, aside from the primitive modes of chemical combination, we need postulate only the additional existence of s–d resonance. It remains to be seen which of these proves to be the more fruitful. Meanwhile, it may be more than a coincidence that high effect appears to radiate from the *intersection* of TM and CD trends, and the inference from this will also need to be taken into account in the development of the ideas.

We conclude with a few remarks on a section of the results which the attack of the discussion has passed by. The diminution of effect if zirconium be substituted for titanium (Table VII), or palladium, platinum, silver and gold for nickel and copper (Table VI; see also certain compositions in Table VIII), is thought to be due to the supplementary operation of a different valency phenomenon, best illustrated by reference to a section of the periodic table (Fig. 9). The elements in the middle of the second and third long periods centred on osmium show high valencies. As valencies decrease towards the flanks and towards the first long period, and knowing that s–d resonance *and* s–d attenuation require low valencies, certainly not more than three, we can understand why any such element substitution will result in a decrease of the area(s) and intensity of the effect zones. Note that the mechanism for high effect, given by the position of the zones, remains; it is the extent of operation which weakens.

## 5. Conclusion

The systematics and electronic structure of another class of compounds can now be understood in principle on a general chemical basis. Refinements to the inferential technique, and the realisation of the loss of simple correspondence between incidence of compound and incidence of effect for transition metal compounds, have enabled subtleties to be resolved which escaped detection in earlier work. A practical consequence is that we have a much clearer idea of the likely provenance of transition metal compounds of high effect, which could be important, for example, in the design of high-performance alloys. The work could also provide the basis for design of alloys on which superconducting films could be formed by thermal oxidation. As regards theoretical considerations, it

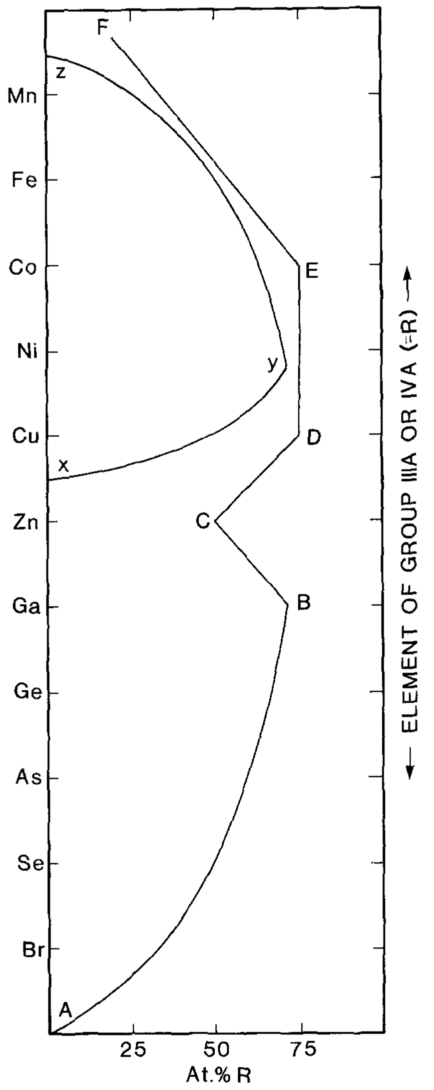

*Figure 8* Envelope of incidence (A to F) for compounds of groups IIIA and IVA with the elements of the first long period: also hyperbolae xy and yz illustrating trends of high effect.

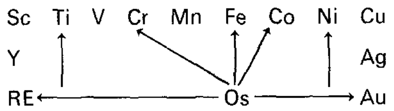

*Figure 9* Part of the periodic table illustrating schematically the diminution of valencies away from a maximum at osmium.

may be no coincidence that lines trending lower left to upper right on the long periodic table join the components of many compounds such as the superconducting perovskites and the heavy fermion type of alloys [9], which are currently of much interest in solid state physics, and it may well be that the present work goes part of the way to providing a general theory of these substances.

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