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THE THEORY OF PHASE FORMATION IN RARE EARTH METAL SYSTEMS

TEORETYCZNE PODSTAWY TWORZENIA FAZ W UKŁADACH METALI ZIEM RZADKICH

The seventeen elements, which make up the rare earth family, consist of two non-$4f$- electron members, Sc and Y, and the fifteen $4f$ electron containing lanthanide elements including La that has an empty localized $4f$ shell. In general, the physical properties, such as the metallic radii, electronegativities, melting points, and crystal structure sequence of the metallic elements, vary in a smooth and regular manner. By utilizing these systematic behaviors, we have learned a great deal about the chemical, metallurgical and physical behaviors of not only the rare earth elements, but also the other elements in the Periodic Table. This includes: (1) the dependence of the entropies of transformation and fusion of the pure metals on the structure and electronic nature; (2) the influence of lattice rigidity on solid solution formation and thus solved one of the oldest metallurgical riddles; (3) the representation of 91 binary rare earth diagrams by a single generalize phase diagram; and (4) the existence of 4f bonding in the lanthanide metals, alloys and compounds well before theorists confirmed this by first principle calculations.

Keywords: rare earths, lanthanides, systematics, alloying theory, thermodynamic properties, solid solution alloys, $4f$ bonding

Na rodzinę siedemnastu pierwiastków ziem rzadkich składają się dwa pierwiastki nie zawierające elektronów $4f$ – Sc i Y, i piętnaście lantanowców w tym La, który posiada pustą zlokalizowaną podpowłokę $4f$. Można ogólnie stwierdzić, że właściwości tych metalicznych pierwiastków, takie jak promienie atomowe poszczególnych metali, elektroujemność, temperatury topnienia oraz sekwencja ich strukturkrystalicznych zmieniają się w sposób ciągły i regularny. Korzystając z tych systematycznych zachowań, poznano wiele właściwości chemicznych, metalurgicznych i fizycznych, nie tylko pierwiastków ziem rzadkich, lecz także innych pierwiastków układu okresowego. Dotyczy to w szczególności: (1) zależności entropii transformacji i entropii topnienia czystych metali od ich struktury krystalicznej i elektronowej, (2) wpływu rodzaju sieci krystalicznej na tworzenie roztworów stałych, które pozwala rozwiązać jedną z najstarszych metalurgicznych niejasności, (3) możliwości przedstawienia 91 wykresów pierwiastków ziem rzadkich za pomocą jednego ogólnego wykresu fazowego, (4) występowania wiązań $4f$ w lantanowcach, ich stopach i związkach potwierdzonych następnie za pomocą teoretycznych obliczeń *ab initio*.

1. Systematics and anomalies – an introduction

The first successful applications of systematics to the rare earth elements goes back to work of D. I. M e n d e l e e v in 1869 who predicted the existence of Sc metal, which was not discovered until 1879 [1]. However, the observations of V. M. G o l d s c h m i d t and coworkers in the mid-1920s was the beginning of the modern day application of systematics to the rare earth elements. These scientists noted that the lattice parameters of the cubic lanthanide R_2O_3 phases decreased with increasing atomic number, and coined the term the "lanthanide contraction" [2]. This contraction is due to the ineffective screening of the nuclear charge by the $4f$ electrons, and as a result, the nuclear charge seen by the outer valence electrons increases as one continues to add a $4f$ electron proceeding along the lanthanide series.

The research by W. K l e m m and H. B o m m e r on the preparation of the rare earth metals and the determination of their crystal structures showed that Eu and Yb had anomalously low densities (i.e. anomalously large atomic volumes) compared to the other lanthanide metals (La to Sm, and Gd to Tm, and Lu) [2], see Fig. 1. They concluded that Eu and Yb are divalent metals, which means that Eu had a half-filled $4f^7$ configuration and Yb had a completely filled $4f^{14}$ shell. These results were a powerful confirmation of Hund's rule that

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half-filled and completely filled electron shells are stable states. The atomic volume densities, melting points and vapor pressures of Eu and Yb are consistent with those of the alkaline earth metals Ca, Sr and Ba, and in analogy with the lanthanides, Eu and Yb along with Ba make up the baride series of elements, and exhibit the "baride contraction" [3].
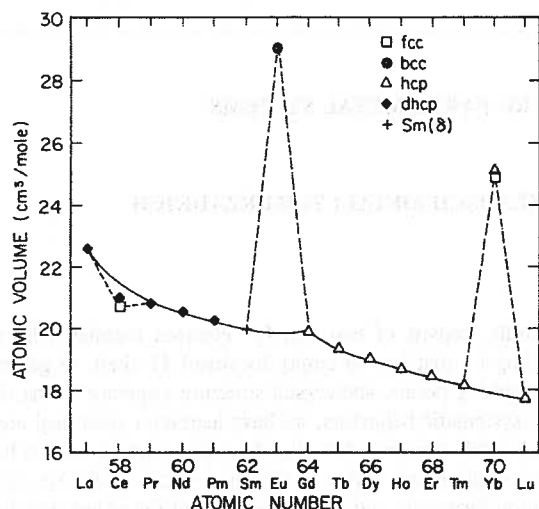

Fig. 1. Atomic volume of the lanthanide metals vs. the atomic number

Thus from the early history of the chemistry and metallurgy of the rare earth elements (especially the lanthanides) we have seen that the interpretations of observations of the physical nature of the pure metals and their compounds has led to new science and verification of some fundamental theories. More recent applications of systematics and anomalies, since the early 1960s, has expanded our knowledge and understanding of these elements. In addition, systematics have been used: (1) to detect (expose) erroneous values, and/or question the exactness and reliability of reported literature results; (2) predict unknown values and properties; and (3) help explain the properties and behaviors of non-rare earth elements, thus expanding our comprehension of the chemistry and physics of all of the elements. A few of the successes are discussed below.

2. Entropies of fusion and transformation

The melting and transformation temperatures of the lanthanide metals are plotted in Fig. 2. The melting point anomalies at Ce, Eu and Yb are quite evident, and again confirm that metallic Eu and Yb are divalent and belong to the alkaline earth family (the melting points are comparable to those of Ca, Sr and Ba – 839, 772 and 725°C, respectively). The anomaly at Ce is due to its mixed valence behavior, $v = 3.06$ [4]. For the normal trivalent

metals, the melting points rise quite sharply with increasing atomic number from 918°C for La to 1663°C for Lu. Furthermore most of the metals transform from a close packed structure [hexagonal close packed (hcp), face-centered cubic (fcc) and double hexagonal close packed (dhcp)] to the body-centered cubic (bcc) allotrope before melting, the exceptions being Ho, Er, Tm and Lu, which are monomorphic.
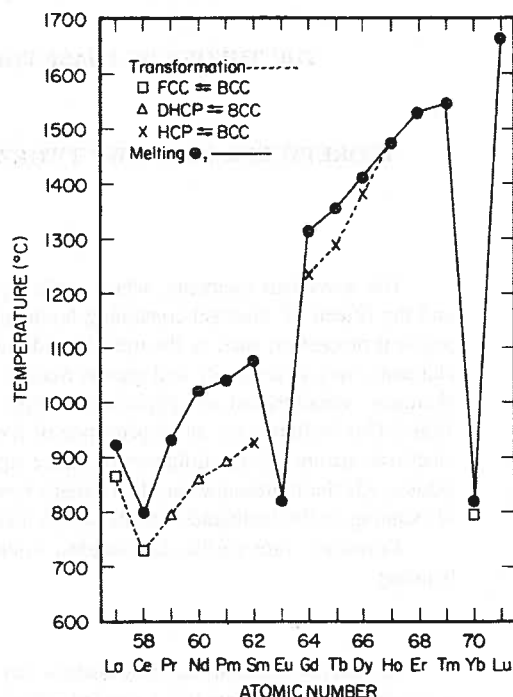

Fig. 2. The melting and transformation temperatures of the lanthanide metals vs. the atomic number

High temperature heat contents, heat capacity, heats of transformation and fusion, and related thermodynamic functions were measured by S p e d d i n g *et al.* [5] (Ce, Nd, and Sm), B e r g *et al.* [6] (Y, La, Pr, Eu, and Yb), and D e n n i s o n *et al.* [7] (Sc, Gd, Tb, Dy, Ho, Er, Tm and Lu). The latter authors found that the entropy of fusion decreased with increasing size of the rare earth metal and that there was an electronic dependence of the heat of transformation. These unusual behaviors prompted a further study of the entropies of fusion and transformation of the metallic elements [8]. It was noted that the entropy of fusion for the hcp metals (2.42 ± 0.16 e.u.) appears to be slightly greater than that for the fcc metals (2.28 ± 0.22 e.u.), both of which are significantly greater than those of the bcc metals (1.68 ± 0.38 e.u.)[1] A closer examination revealed that there was a valency (v) dependence of about 0.165v for entropies of fusion (in e.u.), i.e.

$$\Delta S_F = 1.50 + 0.165v \qquad bcc \qquad (1)$$

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[1] The entropy units (e.u.) values are in cal/mole K.

$$\Delta S_F = 2.10 + 0.165v \qquad fcc \qquad (2)$$

$$\Delta S_F = 2.24 + 0.165v \qquad hcp. \qquad (3)$$

These equations were used to predict the entropy of fusion for 16 metals for which no reliable experimental value was known. Furthermore, it was suggested that the size dependence of the entropy of fusion of the lanthanide was due to a $4f$ hybridization with the valence $(5d6s^2)$ electrons, and thus this f hybridization could account for the low value for U and very low value for Pu (see section 4 below). An analysis of the entropy of transformation values lead to the following observations:

$$\Delta S_{tr} = 0.15 \qquad hcp \rightarrow fcc \qquad (4)$$

$$\Delta S_{tr} = 0.18v \qquad fcc \rightarrow bcc \qquad (5)$$

$$\Delta S_{tr} = 0.15 + 0.18v \qquad hcp \rightarrow bcc, \qquad (6)$$

where v is the valence, and the ΔS_{tr} values are in e.u. These equations were used to predict the entropies of transformation of five metals for which no data exist.

Since the 1975 paper, the experimental values for the entropy of fusion for nine of the sixteen metals have been determined, while for the entropy of transformation, four of the five metals experimental values exist. The experimental quantities are compared with the predicted values in Table 1. It is noted that there is good

TABLE

Comparison of the estimated [8] and experimental values [9] for the entropies of fusion and transformation

Metal	Estimated (e.u.)	Experimental (e.u.)	Percent Difference
Entropy of Fusion			
Be	1.85	1.92	3.8
Ti	2.2	2.05	-6.8
V	2.35	2.52	7.2
Zr	2.2	2.11	-4.0
Hf	2.2	2.60	18
Ta	2.35	2.46	4.7
Ir	2.6	2.29	-12
Th	2.2	1.63	-26
Np	1.1	1.37[a]	-24
Entropy of Transformation			
Be	0.51	0.39	-23
Sr	0.36	0.23	-36
Hf	0.87	0.70	-20
Th	0.72	0.53	-26

[a] The experimental value was calculated from the heat of fusion and the melting point given by Ref. [10].

agreement for most of the metals for the entropies of fusion. The two notable exceptions are the $5f$ elements Th and Np, and this is consistent with the low values for the light lanthanides and for U and Pu as noted above.

The estimated values for the entropies of transformation are consistently much larger than the experimental values, differing by 20 to 30% (Table 1). However, the numerical difference is generally less than 0.2 e.u., but the small magnitude of the entropies results in large percentage differences, and the agreement can be considered to be fair.

3. Terminal solid solutions

The solid solubilities of the rare earth metals with themselves $(R - R')$, the rare earth metals in non-rare earth metals (R in M), and the non-rare earth metals in the rare earth metals (M in R) were extensively studied over a 20 year period from the mid 1960s to the mid-1980s [2]. Of these studies, the investigation of the solid solubility of the lanthanide metals in Ag [11] and Au [12] helped to answer one of the oldest unsolved riddles known to metallurigists, i.e. why Cu and Au form a continuous solid solution but Cu and Ag do not. The solid solubilities of R in Ag and in Au ranged from ~0.1 at.% to ~8 at.%: the solubility was essentially constant at ~0.1 at.% for the large size light lanthanides (La to Sm), and then started to increase for the small size heavy lanthanides rising from ~1 at.% at Gd to 8 at.% at Lu. However, in every case the solid solubility of R in Au is larger than that of R in Ag. Since most of the properties governing the formation of terminal solid solutions (size, valence, electronegativity) are essentially identical for Ag and Au it was difficult to understand why there was this difference in solid solubilities. A clue came from a study of the solid solubility of Mg in R [13] which was carried out during the same time period as the R-Au and R-Ag investigations were being conducted. In the R-Mg study, Joseph and Gschneidner pointed out that the lattice rigidity of the solvent needed to be taken into account in order to explain the observed variation of the solubility of Mg in R along the lanthanide series. That is, a solvent with a less rigid lattice (a low Debye temperature, Θ_D) would be expected to dissolve more of a solute (impurity) than a solvent with a more rigid lattice (a high Θ_D). Since Θ_D of Ag (228 K) is significantly larger than the Θ_D of Au (165 K), one would expect that Au as a solvent would dissolve more of an impurity atom, than would Ag, and that is what just observed in the R-Au vs. R-Ag terminal solid solutions, comparing the same R element. Now, we can understand why Cu and Au form a continuous solid solution from pure Au to pure Cu, and why Cu and Ag form two extensive but not

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continuous solid solutions with an intermediate eutectic between them. Thus, we see that without using the rare earths as a research tool, we still might not have realized even today that the lattice rigidity is an important factor which needs to be considered in the alloy theory of solid solution formation along with the size, crystal structure and electronic structure of the solvent and solute [14].
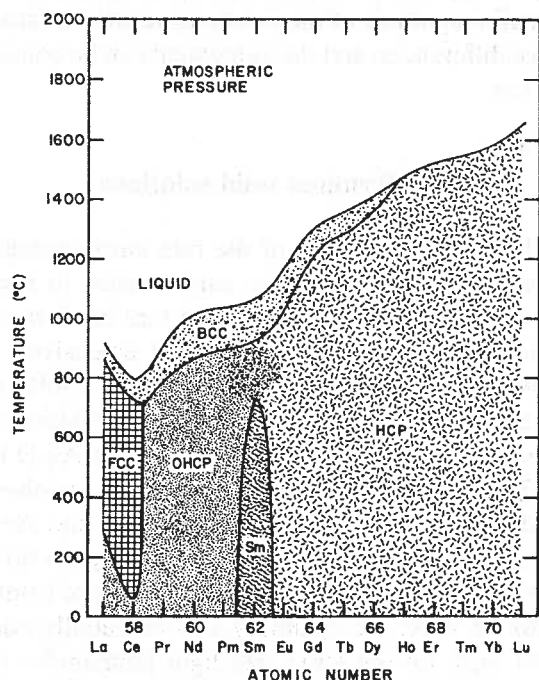

Fig. 3. Generalized phase diagram for the trivalent intra-lanthanide alloys

As one might expect, the rare earth metals form extensive solid solutions when alloyed with another rare earth, as long as the valences are the same. However, the rare earth metals, as noted in section 2, crystallize in several different crystal structures: fcc, dhcp, the Sm-type structure, hcp and bcc. Complete miscibility, of course, can only occur if the end members have the same crystal structure. But in most cases, at least below the close packed structure – bcc transformation temperature, the solid solutions regions terminate. It is noted that there is a systematic occurrence of the crystal structures as one proceeds along the lanthanide series from fcc to dhcp to the Sm-type to hcp [2]. Early work in the 1960s indicated that $4f$ bonding was an important parameter in determining which structure was formed [15, 16]. On the basis of this early work and 30 reasonably well established $R-R'$ phase diagrams a generalized phase diagram (Fig. 3) was proposed to represent 91 possible individual intra *trivalent* rare earth metal binary phase diagrams [17, 18]. The Sc-R phase diagrams were not considered in establishing this generalize phase diagram, primarily because the metallic radius of Sc is significantly smaller than that of Lu, the smallest lanthanide – 1.641 vs. 1.735 Å. In

addition it was shown that there are 13 possible types of binary $R-R'$ phase diagrams, two of which have not been experimentally verified.

The pressure dependence of the one atmosphere generalized phase diagram was also proposed [18, 19]. Generalized phase diagrams at 1, 2 and 4 GPa (10, 20 and 40 kbars) show that pressure expands the bcc, fcc and the Sm-type phase regions, and reduces the dhcp and hcp regions across the lanthanide series. Also a plot of the crystal structures at room temperature as a function of pressure across the lanthanide series up to 24 GPa (240 kbars) was constructed. Shortly thereafter, this 25°C isothermal section was extended up to 50 GPA (500 kbars) [20].

4. $4f$ bonding or two kinds of $4f$ electrons

The unusual crystal structures (dhcp and the Sm-type) and crystal structure sequence in the lanthanide metals both at atmospheric pressure and high pressure, as noted above, along with their (1) anomalously low melting points (especially those of the light and middle lanthanides, see Fig. 2), (2) heats of sublimation and (3) bond energies relative to the corresponding properties of the Group 1 (K, Rb, Cs), Group 2 (Ca, Sr, Ba), Group 3 (Sc, Y) and Group 4 (Ti, Zr, Hf) elements led to the conclusion that $4f$ bond hybrids are involved in the chemical bonding [15, 16, 21]. In the 1971 paper Gschneidner [21] stated that: "The two main points which are being emphasized are the following: (1) The lanthanide metals, other than Lu and perhaps Er and Tm, have two kinds of $4f$ electrons, the atomic $4f$ and the band or bond $4f$ electrons. (2) This dual $4f$ electron model enables one to explain, at least qualitatively, the crystal structure sequence, the melting points and heats of sublimation of the lanthanides. Heretofore, one model has never been able to explain all three of these properties, although plausible models which do not involve $4f$ electrons, can be used to explain each of these properties alone."

This model was re-affirmed in 1993 when systematics was applied to other physical properties and chemical behaviors of the pure metals (the elastic moduli of R, and the solid solubilities of H in R, and of R in Au) and the heats (free energies) of formation of Sc, Y and lanthanide compounds (R_2O_3, RF_3, RS, RMg and RIn_2) [22], showing that $4f$ bonding was the only reasonable explanation of the observed chemical and physical properties of the lanthanides. In the same year, a group of theorists reported that by using first principle calculations the $4f$ bond in Pr metal was strongly hybridized with the s, p and d bond electrons because the first empty $4f$ level is located close enough to the Fermi level that it mixes with the normal valence electrons [23]. This

model (of electrons in the first empty $4f$ level hybridizing with the $6s$, $5d$ band electrons while the normal $4f$ levels associated with a given lanthanide lie below the Fermi level and are fully occupied as expected for the corresponding trivalent lanthanide ion [e.g. f^2 for Pr, f^7 for Gd, etc.] [see Fig. 4]) solidified our understanding of the nature of $4f$ bonding. More recently, first principle calculations of the bonding in the lanthanide metals [24] sulfides [24, 25] and oxides [26] confirmed the two kinds of $4f$ electrons model (localize core-like and delocalized band-like).
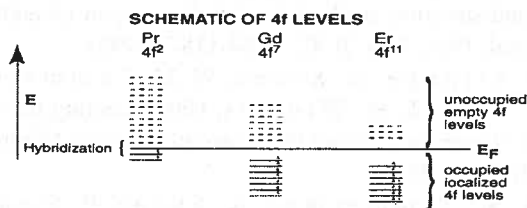

Fig. 4. A schematic of the $4f$ levels in three representative *trivalent* lanthanide metal atoms

5. Summary

There are two sets of systematic trends in the rare earth group of elements – (1) the variation from Sc to Y to Lu and how the lanthanide fits this trend; and (2) the variation in the lanthanides from La to Lu exclusive of Sc and Y. Examination of both trends either separately or in combination has contributed much to our understanding not only of the rare earth metals themselves but also to science of the entire Periodic Table. A study of high temperature thermodynamic properties of the rare earth metals led to the development of a method to predict the entropies of the common metallic transformations (fcc or hcp to bcc) and of fusion. Investigations of the terminal solid solubilities of R in M or M in R, showed that lattice rigidity plays an important role in determining the extent of the solid solution region, and solved a longstanding enigma concerning the difference in the Cu-Au and Cu-Ag systems – complete solid solubility vs. terminal solid solutions with an intermediate eutectic, respectively. The application of systematics to the chemical, metallurgical and physical behaviors of rare earth materials lead to the conclusion that $4f$ electrons must be involved in the bonding, but it is the few electrons that occupy the empty $4f$ levels just above the Fermi level which hybridize with the $6s$ and $5d$ valence electrons. The $4f$ electrons in the $4f$ levels below the Fermi energy account for the normal magnetic and optical properties associated with lanthanide materials – i.e. there are two kinds of $4f$ electrons.

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