

# Systematics in lanthanide and actinide solids

K.A. Gschneidner, Jr.

*Ames Laboratory and Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011-3020, USA*

## Abstract

Generalized phase diagrams have been available for about ten years for both the lanthanides and actinides, and these have proven to be quite useful in understanding the phase relationships in the two series of elements and in predicting the existence of phases when experimental data are lacking. The two generalized phase diagrams are examined for their similarities and differences. The application of systematics in lanthanide compound series has been useful in predicting crystal structures (phase relationships), melting points, and enthalpies and free energies of formation. Analyses of these data indicate that there is 4f hybridization with the other valence and/or bonding electrons. It is most likely that the 4f hybridization involves the empty 4f level(s) just above the Fermi surface and not the filled localized 4f levels. Systematics has also been applied to the actinide metals. Since the experimental data are primarily limited to Th, U and Pu, and since the valence changes from 3 to 7 in the early actinides, the usefulness of these techniques, which have been so successful for the lanthanides, has been limited. If more experimental data were available for actinium and its alloy systems, much more progress could be made in our understanding of actinide alloys and compounds. In addition, as a result of applying systematics, it is thought that the lattice parameters reported for Ac and AcH<sub>2</sub> are quite likely to be wrong. It is proposed that the correct lattice parameter for f.c.c. Ac metal is 5.670 Å, about 6.7% larger than the value which has been accepted up to now.

*Keywords:* Systematics; Lanthanide solids; Actinide solids

## 1. Generalized phase diagram

Generalized phase diagrams have been proposed for both intra-lanthanide [1] and intra-actinide [2] phase diagrams, and these have proven to be quite useful in understanding the phase relationships in the two series of elements and in predicting the existence of phases when experimental data are lacking, especially in the lanthanide series. The generalized phase diagram for the trivalent lanthanides is shown in Fig. 1. This single diagram, which is also valid for yttrium–lanthanide binary alloys, represents a total of 91 binary phase diagrams. The systematization number shown at the top of the figure is used to calculate the critical points and phase boundaries for any combination of the trivalent lanthanide metals for which no experimental data exist. Indeed, two such calculated diagrams, La–Er and Sm–Ho, have been presented by Gschneidner [1] in his classification of the intra-lanthanide binary systems into the 13 possible types of phase diagram that could form between the trivalent lanthanides. The representation of 91 possible binary alloy phase diagrams in a single diagram is possible because of the regular and

systematic variation of the physical properties, such as the metallic radius (see Fig. 2), melting points, etc. of these elements. One notes, significant anomalies in the radii of the lanthanides (which also are evident in other physical properties) for  $\alpha$ -Ce, Eu and Yb. Eu and Yb have anomalous radii and physical properties because they are divalent in their room temperature metallic states. Because of this, the generalized phase diagram shown in Fig. 1 cannot be used to estimate intra binary alloy phase diagrams involving these divalent metals. However, it can be used to estimate the alloying behavior of hypothetical trivalent Eu and Yb. Furthermore,  $\alpha$ -Ce is also excluded from the generalized phase diagram, because this phase exists only at high pressure (above 0.7 GPa) at 298 K, or below about 120 K at 1 atm. The other Ce phases ( $\beta$  and  $\gamma$ ) have a valence close enough to three, that Ce can be treated as a normal trivalent lanthanide in the generalized phase diagram.

The more-or-less generalized phase diagram for the actinide metals is shown in Fig. 3. This diagram is quite different from that for the lanthanides. Indeed, it was constructed by Smith and Kmetko [2] by connecting the known binary phase diagrams (Np–Pu, Np–U and

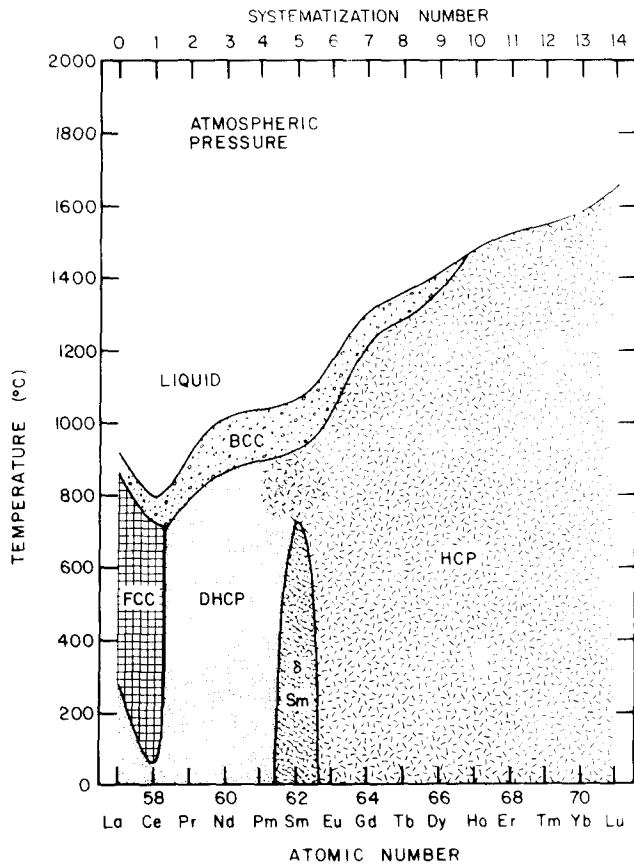


Fig. 1. Generalized phase diagram for the trivalent intra-lanthanide alloys (after Gschneidner [1] by permission of *J. Less-Common Met.*).

Pu-U) and the known elemental phase transformations and melting points to give seven individual, but connected, phase diagrams. Furthermore, from the known Pu-Th and Th-U phase diagrams, it was clear that these seven individual diagrams could not be compressed into a single generalized phase diagram as was done for the lanthanides. This becomes even more obvious when one examines the metallic radii and the approximate valences of the actinide elements shown in Fig. 2. Instead of a 7.6% decrease in radii from La to Lu, one finds a 19.8% change between Ac and Np; and instead of constant valence of 3 for the lanthanides, it varies from 3 (Ac) to 7 (Np) for the light to middle actinides. Just as for the lanthanides, where the divalent lanthanides Eu and Yb cannot be included in the generalized phase diagram for the trivalent lanthanides, one should not expect to be able to compress the actinide phase diagrams into one diagram when one finds a different valence for each of the early actinides. Thus, for the lanthanides, it is easy to take the appropriate ratio of two elements to mimic one which lies between them (except for those properties which directly depend on the specific 4f electronic configuration, i.e. optical and magnetic properties). For example, a 30at.%La-70at.%Gd alloy would mimic pure Sm [1]. In the actinide series because of the valence

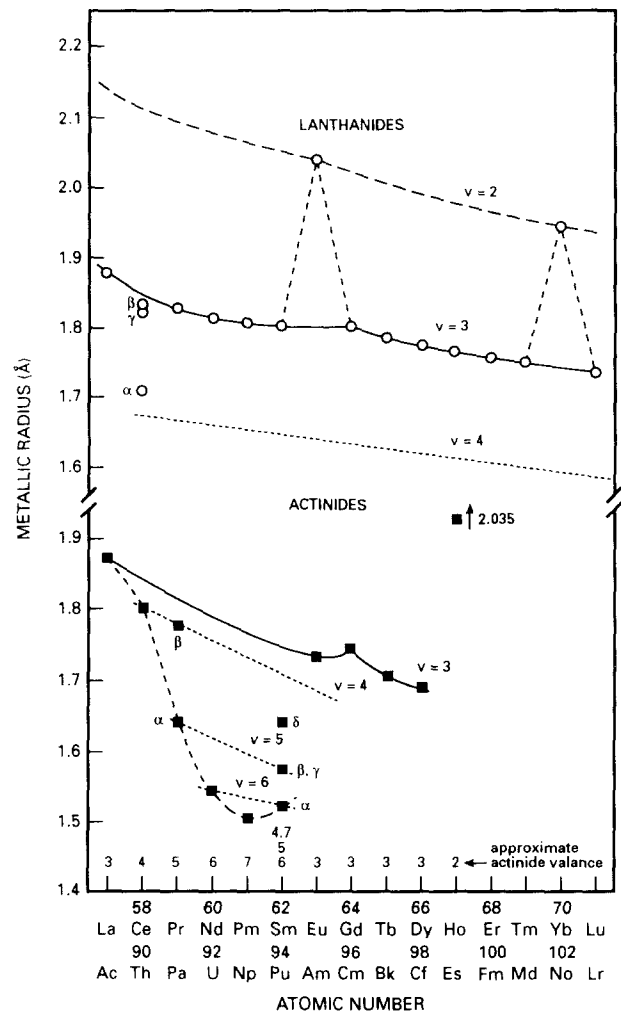


Fig. 2. Metallic radii for a coordination number of twelve of the lanthanide and actinide elements. This plot assumes that the experimental value for the lattice parameter for Ac as reported by Farr et al. [4] is correct. Also see Fig. 5 and comments in the text.

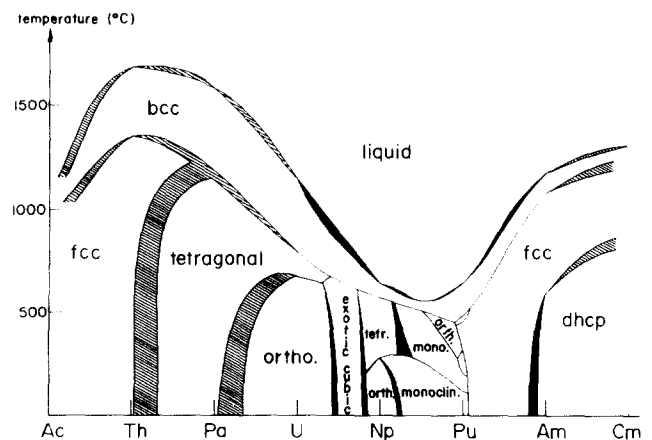


Fig. 3. Generalized phase diagram, formed by connecting the binary alloy phase diagrams, for the light actinides (after Smith and Kmetko [2] by permission of *J. Less-Common Met.*).

differences of the components, it is unlikely that an alloy of the appropriate composition would mimic an element which lies between them. However, some systematics can be found in some intra-actinide systems. For example, both U–Np and U–Pu alloys form the “exotic cubic” phase shown in Fig. 3 between U and Np; and as predicted from the generalized actinide phase diagram, the alloy composition of this phase is found to lie closer to Np than it does to Pu in the respective U systems.

It should be noted that for the heavy actinides (Am through Cf), since they have essentially the same valence, a generalized phase diagram, similar to the lanthanide diagram, could be used to describe their (Am through Cf) alloying behaviors and to predict their intra-actinide phase diagrams. Unfortunately, the paucity of data does not permit one to construct such a diagram.

The major difficulty in applying systematics for the actinide group as a whole is, however, the lack of experimental data among the actinide elements and their binary intra-actinide alloys – only six diagrams are known.

Another problem in developing actinide systematics is the radius of actinium: it appears to be too small relative to that of Th. The change in radius on going from trivalent Ac to tetravalent Th is much too small when one compares the shifts of the radii due to valence changes for the lanthanide series from 2 to 3 and 3 to 4, with the valence changes in the actinide series on going from 3 to 4, 4 to 5, and 5 to 6. That is, the reported radius would suggest Ac has a valence greater than 3, which is impossible since it would involve removing an electron from the Rn rare gas core level to attain this higher valence. Zachariasen [3] had recognized this problem over 20 years ago, and used a hypothetical value of 1.977 Å for trivalent Ac, while at the same time he ignored the experimental value of 1.877 Å (as used in Fig. 2). The Zachariasen value for Ac is consistent with these valence changes, and this would imply that the radii for Am, Cm, Bk and Cf are more appropriate for a valence of about 3.5, instead of 3 as shown in Fig. 2. In checking the original paper by Farr et al. [4], it is noted that their Ac sample weighed about 0.01 mg and could have easily been contaminated. Indeed, they report the existence of two f.c.c. patterns in their X-ray films, in addition to KCl lines, one of which had a lattice parameter of 5.311 Å and the other a parameter of 5.670 Å. They ascribed the first to Ac metal and the second to AcH<sub>2</sub> for reasonable arguments presented in their paper. If, however, the larger lattice parameter were that of Ac metal, then its radius would be 2.005 Å, quite close to the Zachariasen hypothetical value of 1.977 Å, but then one would have to explain the observed smaller lattice parameter.

There have been some reports that an f.c.c. pattern has been observed in X-ray patterns of some lanthanide metals (in the case of f.c.c. Ce metal two f.c.c. patterns) [5,6], and that the radius, which was calculated from the lattice parameter, is smaller than the radius of the corresponding pure lanthanide metal. This f.c.c. pattern has been ascribed to the monoxide [5,6]. The existence of a material having a smaller f.c.c. lattice constant is probably correct, but it is doubtful that it is a “monoxide” – it might be due to the presence of several interstitial impurities (i.e. H, C, N, O) acting together which cause this f.c.c. phase to form [6]. Clearly there is still a lot to be learned even for the lanthanide metals.

Further evidence supporting the larger lattice parameter for Ac metal is the fact that the lattice parameters for all of the known Ac compounds are about 3.0% larger than those of the corresponding isostructural La compounds [7,8]. This includes the compounds R<sub>2</sub>O<sub>3</sub> and R<sub>2</sub>S<sub>3</sub> [7], and RF<sub>3</sub>, RCl<sub>3</sub>, RBr<sub>3</sub>, ROF, ROCl, ROBr and ROP<sub>4</sub>·½H<sub>2</sub>O [8], where R ≡ Ac or La. The lattice parameter of f.c.c. Ac (*a* = 5.670 Å) is 6.9% larger than that of f.c.c. La, which is reasonable since the atomic fraction of Ac (or La) in the various compounds ranges from 0.17 to 0.40, and one would expect smaller increases in the lattice parameters in the compounds owing to this dilution effect.

Finally, the last piece of evidence supporting the larger lattice parameter being the true value for Ac is found in the systematic variation in the metallic radii in the group IIA, IIIA and IVA elements, as shown in Fig. 4. As one observes, for each group the radius increases smoothly as the period (or the atomic number) increases within the group, provided the “new” Ac radius value is used, rather than the “old” Ac value (see figure caption for definition of “old” and “new”) for the group IIIA elements. The “old” value obviously is anomalous with the trends observed in groups IIA and IVA. This is true, in spite of the lanthanide contraction, which is seen as the difference between the La and Lu values, and which accounts for the low value of Hf relative to Zr. That is, the lanthanide contraction could not account for a low value for Ac, because if this were the case both the Ra and Th values should also be low and they are not. Apparently, the influence of the lanthanide contraction is washed out by the time a sufficient number of electrons have been added to the elements to reach the next period of elements (the 7th starting with Fr). The radius for hypothetical tetravalent Ce shown in Fig. 4, indicating the approximate size of the “lanthanide” contraction for the group IVA metals, i.e. Ce(4), is the starting element and Hf is the end member.

Based on this evidence we have assumed that the reported lattice parameter of Ac is incorrect, and that the X-ray pattern corresponding to the larger f.c.c. lattice constant is not AcH<sub>2</sub> but is indeed that of Ac

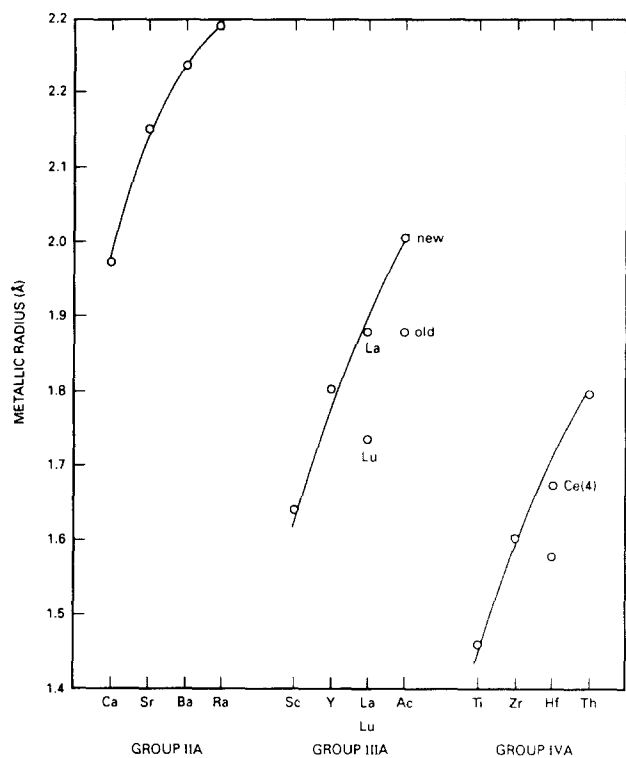


Fig. 4. Metallic radii of the groups IIA, IIIA and IVA metals. The value labeled "old" for Ac is the radius calculated from the value of the lattice constant reported by Farr et al. [4], while the value labeled "new" is the radius calculated from the lattice parameter which is proposed here to be the correct value for Ac metal. The value labeled "Ce(4)" is the radius for hypothetical tetravalent cerium metal [9].

metal. Using this lattice parameter to calculate the radius of Ac, and replotting the metallic radii vs. atomic number for the actinides (Fig. 5) we find a much more reasonable change in radii on going from a valence change of 3 to 4 from Ac to Th. In making this change we also have to reassign the valences of Am, Cm, Bk and Cf from 3 (as listed in Fig. 2) to 3.8, 3.6, 3.8 and 3.8 respectively.

However, if the smaller radius of Ac were correct, then the nature of  $5f7s6d$  hybridization in the actinide metals is not well understood, and would appear to be anomalous with respect to all that we know about bonding in the rest of the periodic table. Thus, it is critical that the crystal structure and lattice parameter of actinium metal be redetermined. The radius of actinium is the keystone which is necessary to carry out systematization studies of the actinide metals, alloys and intermetallic compounds.

If one were to redetermine the lattice parameter of Ac, it is possible that because of the reactivity of Ac, one would again find two f.c.c. patterns, and one would face the same dilemma as encountered by Farr et al. [4]. This is not correct, however, since X-ray intensity data, even semi-quantitative, will allow one to determine which pattern is due to pure Ac metal and which is

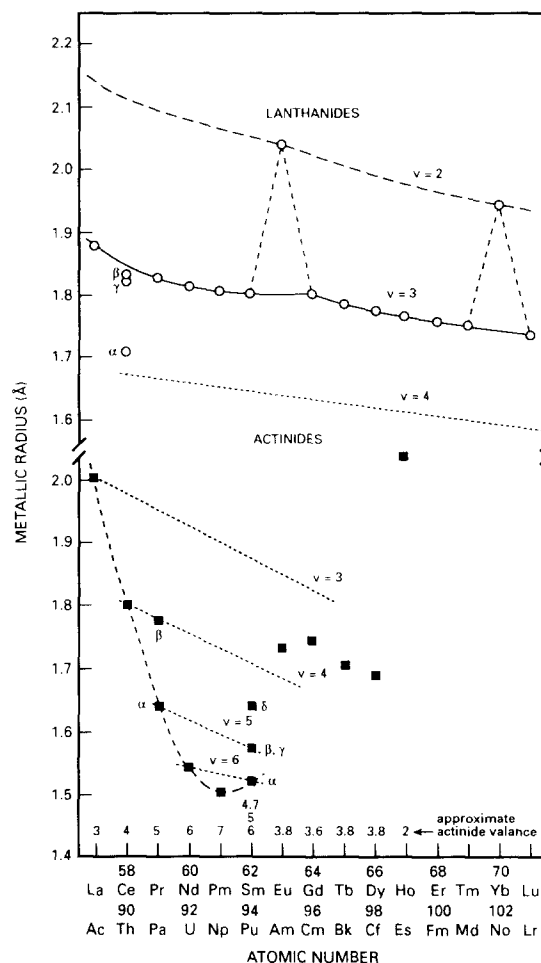


Fig. 5. Metallic radii for a coordination number of twelve of the lanthanide and actinide elements. This plot is based on the reinterpretation of the reported Ac X-ray crystal structure and lattice parameter data (see text). All of the radii shown in Figs. 2 and 5 are the same, except for Ac.

due to the impurity stabilized phase. As noted by Gschneidner and Waber [6], a quick visual check to see which neighboring line, the (331) or (420), is the more intense will give the answer: in the pure metal the (331) line is more intense than the (420) line, while in the impurity stabilized f.c.c. structure the (420) line is more intense than the (331) line. (Note: one does not need to use a modern diffractometer with an electronic intensity counter to do this, the human eye is an excellent differential photometer – all one needs to determine is which line is more intense than its neighboring line.) Other intensity ratios [6], if they can be measured, may also be used to add confidence to one's conclusion. In addition, one should hydrogenate the Ac metal to form  $AcH_2$  and then determine its lattice parameter, which we expect to be about 6.06 Å.

## 2. Systematics

Systematics is a powerful tool for understanding the physical and chemical nature of materials. As noted above, in the case of the radius of Ac, anomalies can point to possible erroneous experimental data, which need to be verified as being anomalous, or as being correct. In the former case, i.e. verification of the anomaly, this means that our idea(s) or explanation(s) are not correct and need to be modified to account for the apparent anomaly. This in turn improves our knowledge and comprehension. In addition, systematics allows one to predict properties and behaviors with a reasonable confidence level in the absence of experimental data. The application of systematics to the rare earth elements has been highly developed over the last 70 years [10,11]. The occurrence of so-called anomalies, at the time, has led to what later was considered fact and normal behavior. These include the lanthanide contraction, the divalent metallic states of Eu and Yb, and valence fluctuation behaviors in Ce and Yb systems. As shown recently, more information and enlightenment can be obtained if one also utilizes Sc and Y together with the lanthanide elements [11]. In a comprehensive review of the physical properties of the rare earth metals – the formation and solid solubility range of solid solution alloys; the melting behavior and the heats (free energies) of formation of compounds; and aqueous solutions – Gschneidner [11] has demonstrated by using systematics that 4f hybridization with valence electrons (5d,6s) of the lanthanide atom, and with those of the non-rare earth element in alloys and compounds occurs. In many cases evidence is presented which indicates that the 4f hybridization involves not only the first few light lanthanides but also the heavies. This 4f hybridization is difficult for many scientists to accept, especially since there is strong evidence that the 4f electron is localized from magnetic and optical measurements. The solution to this dilemma was apparent from the band structure calculations of Temmerman et al. [12], who found that unoccupied 4f bands in Pr metal hybridized strongly with the s, p and d bands. That is, the first empty 4f level in the various lanthanide metals is close enough to the Fermi level that it mixes in with the normal valence electrons to give rise to the anomalies seen in the systematics of the various properties studied. Our problem, until the publication of the paper by Temmerman et al., was that everyone was focusing on the occupied 4f levels and forgetting about the empty 4f level(s).

Application of systematics to the actinides is not nearly as far advanced as for the lanthanides (rare earths), primarily because of lack of information owing to the limited availability of many of the actinide elements and their radioactive nature. The other problem, as noted above, is the changing valence as one

proceeds along the actinide series, and also the fact that the elements can exhibit several different valence states in their bonding to form various metallic and non-metallic compounds. The state-of-the-art concerning the phase relationships and the thermodynamic properties has recently been summarized by Colinet and Pasturel [13] and the reader is referred to their comprehensive summary for details. Basically, most of the known information is for Th, U and Pu alloys and compounds, only some scattered data are known for the remaining actinides. From their analyses they find that the free energy of formation for compounds formed between the non-transition metals and the three actinides becomes less negative in the sequence Th, Pu and U, while for compounds formed between transition metals and these actinide metals, they become less negative in the sequence Th, U and Pu, i.e. the positions of U and Pu change.

Although it would be desirable to have much more information on the other actinides (in addition to Th, U and Pu), the key element is Ac, since it is the first element of the series. In addition to serving as a starting point (anchor) for the systematic behavior along the actinide series, the Ac data could also be tied in with those for Sc, Y, La and Lu, and presumably one could extract much more information and knowledge using the non-magnetic rare earth elements in the systematization studies of the actinide metals, compounds and alloys.

## References

- [1] K.A. Gschneidner, Jr., *J. Less-Common Met.*, 114 (1985) 29.
- [2] J.L. Smith and E.A. Kmetko, *J. Less-Common Met.*, 90 (1983) 83.
- [3] W.H. Zachariasen, *J. Inorg. Nucl. Chem.*, 35 (1973) 3487.
- [4] J.D. Farr, A.L. Giorgi, M.G. Bowman and R.K. Money, *J. Inorg. Nucl. Chem.*, 18 (1961) 42.
- [5] K.A. Gschneidner, Jr., *Rare Earth Alloys*, van Nostrand, Princeton, NJ, 1961, p. 240.
- [6] K.A. Gschneidner, Jr., and J.T. Waber, *J. Less-Common Met.*, 6 (1964) 354.
- [7] P. Villars and L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, Vol. 1, American Society for Materials International, Metals Park, OH, 1991, p. 481.
- [8] S. Fried, F. Hagemann and W.H. Zachariasen, *J. Am. Chem. Soc.*, 72 (1950) 771.
- [9] K.A. Gschneidner, Jr., and R. Smoluchowski, *J. Less-Common Met.*, 5 (1963) 374.
- [10] K.A. Gschneidner, Jr., and A.H. Daane, in K.A. Gschneidner, Jr., and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 11, North-Holland, Amsterdam, 1988, p. 409.
- [11] K.A. Gschneidner, Jr., *J. Alloys Comp.*, 192 (1993) 1.
- [12] W.M. Temmerman, Z. Szotek and W. Winter, *Phys. Rev. B*, 47 (1993) 1184.
- [13] C. Colinet and A. Pasturel, in K.A. Gschneidner, Jr., L. Eyring, G.H. Lander and G.R. Choppin (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 19, North-Holland, Amsterdam, 1994, p. 479.