

COMMENTS ON THE PAPER *) "RELATIVE STABILITY
OF VARIOUS STACKING ORDERS
IN CLOSE-PACKED METAL STRUCTURES" **)

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In a recent paper, Havinga, Van Vucht and Buschow ¹⁾ (henceforth to be referred to as the authors) presented an interesting explanation for the stacking sequence in metals and intermetallic compounds. The authors are commended for their work, since it is a significant and an important step in our understanding of the occurrence of crystal structures in metals and alloys. There are, however, several comments that I should like to make regarding some of the authors' statements plus one pertinent observation.

The authors state that the treatment of Gschneidner and Valletta ²⁾ is incomplete since it uses short-range interactions due to the $4f$ electrons. This is true if only $4f$ electrons are involved in the bonds, but such is not the case. If one extends the treatment of Altmann, Coulson and Hume-Rothery ³⁾ to determine which $4f$ hybrids have the proper symmetry and the method of Pauling ⁴⁾ to determine which hybrid has the highest bond strength, it is found that the d^3f^3 hybrid will account for the binding in a face-centred cubic lattice and the $(df^5)^m(df^2)^n$ hybrids, where $m + n = 1$, $m > 0$ and $n > 0$, for the hexagonal close-packed structure. Long-range interactions could arise from the d participation in the bond hybrids. Thus, it is somewhat premature to rule out the $4f$ model on this basis.

The authors point out that the $4f$ contribution to the bonding is a small energy contribution. This is a good point, of which we are aware, and which was discussed in a paper presented at the Colloque International sur Les Éléments des Terres Rares in Paris in May, 1969 ⁵⁾. Unfortunately, this paper has not yet been published. In essence, when a material can adopt either one of two different crystal structures, one must consider *all* energy terms, large or small. The question one asks is: "Which energy term, a large, a small, or an intermediate one, determines the structure?" In the case of the rare earths, this is not a simple question to answer. For example, a large energy term may be constant or change only very slightly on an absolute scale from one lanthanide to another in the critical region (the elements and their neighbours where the

*) See E. E. Havinga, J. H. N. van Vucht and K. H. J. Buschow, Philips Res. Repts 24, 407-426, 1969.

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crystal structure changes) in the lanthanide series, while a small energy term may vary enough in the critical region to actually determine which structure is formed. In all likelihood, it is not one, but a combination of several terms which actually has the most influence. Therefore, one is not justified in discarding a contribution just because it is small.

Havinga, Van Vucht and Buschow also point out that La and Y behave similarly to the lanthanide metals, suggesting that the 4*f* electrons do not play a role in determining the structures adopted by the rare-earth metals and their intra rare-earth alloys. This point, however, was thoroughly discussed in the original paper by Gschneidner and Valletta²⁾ on p. 479, and there is no need to repeat their arguments here.

There is one very important fact which the authors have overlooked, i.e., the crystal-structure sequence of the lanthanide metals and their intra alloys at high pressure. *To date there is no model, other than the 4*f* model of Gschneidner and Valletta²⁾, which can explain the sequence of structures observed at high pressure.* Thus the importance of any model concerning the crystal-structure sequence in the 4*f* metals and alloys will be determined by how well it can explain the observed structures not only at atmospheric pressure but also at high pressure.

In conclusion, I should like to point out that even if the 4*f* electrons play a role in determining the crystal-structure sequence in rare-earth materials, this does not exclude the authors' model from also playing a role. The point in fact is, although an individual scientist may have his personal opinion, we do not *know* whether both, one, or neither of these models are important. Unfortunately, the true answer will not be known until exact calculations from first principles, without any approximations, have been carried out. Until that time, further knowledge must come from well-planned and well-executed experiments and other theoretical calculations and models.

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