**TOPOLOGY OF LOCAL ATOMIC ENVIRONMENTS:
IMPLICATIONS FOR MAGNETISM AND SUPERCONDUCTIVITY**

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Wigner-Seitz cells have been constructed, as a function of atomic size, for a number of transition-metal alloys, and a disclination network has been obtained from these. Magnetism in these alloys can be related to the disclination lines, much like the superexchange paths familiar in the magnetism of salts.

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Wigner-Seitz (i.e. Voronoi or Dirichlet) polyhedra, which are a measure of the local atomic environment around atomic sites in solids, usually have 4, 5, and 6-edged faces. The number of edges on a face is a count of the number of nearest neighbors which the central atom in the polyhedron has in common with the neighboring atom responsible for the particular face. The sixfold faces generally involve the nearest of the near neighbors (when distances are measured with respect of the sum of constituent atom atomic radii) and the bond lines associated with these faces are known as major ligands. As noted [1] by Nelson, these major ligand lines may also be viewed as negative disclinations. The purpose of this paper is to suggest that the occurrence of a substantial magnetic moment at an atomic site in certain classes of magnetic systems can be related to the occurrence of major ligand lines to that site. Particular reference will be made to the hard magnets. If only because of the closeness of approach, these major ligands are expected to involve the strongest chemical bonding.

Recently we were considering [2] the α and β Mn structures. In α Mn there appears to be antiferromagnetic coupling along disclination lines. Those sites where all of the faces of the

Wigner-Seitz cell were 5-sided lacked significant magnetic moments. β Mn, which is not believed to order magnetically (except perhaps at very low temperatures), also lacks major ligands. The major ligand lines would thus appear to be in some ways analogous to the exchange and superexchange paths important to the magnetism of transition-metal salts. It is clear that major ligands are not the cause of magnetism in metals. There are, after all, no major ligand lines in hcp Co or fcc Ni. In the case of the rare earth-transition metal hard magnets of concern here, one must ultimately disentangle the effects associated with the ferrimagnetism of the heavy rare earth element compounds from the ferromagnetism of the light rare earth element compounds. The observation to be made here concerning the ferromagnetic systems suggests that their disclination lines are important to their magnetic properties.

Disclination lines may also be important to superconductivity: the linear chains of transition metal atoms in the A15 structures (i.e., in compounds such as Nb_3Sn) are thought to be essential to the superconductivity in these systems; these chains are, in fact, lines of negative disclinations. Some years ago, Frank and Kasper [3] explored a class of crystal structures

where one requirement was that there were lines or sets of disclinations extending across the crystal. The A15 as well as the Laves and σ phases are examples of these. The atomic sites in these structures are 12, 14, 15 and 16-fold, coordinated with 0, 2, 3 and 4 negative disclinations, respectively. The associated Voronoi polyhedra are then (0,0,12), (0,0,12,2), (0,0,12,3) and (0,0,12,4). [Notation: (a,b,c,d,...) indicates a polyhedron having a faces with 3 edges, b with 4, c with 5, d with 6, etc.] In general, the sites without major ligands, (0,0,12), are occupied by the smaller alloy constituents, such as Fe, Co and Ni, whereas the sites with major ligands contain the larger (nonmagnetic) atoms. This may be at the root of the relatively weak magnetism in the Laves phases and the generally weak magnetism which typifies these and the other Frank-Kasper phases.

We have constructed the (modified) Voronoi polyhedra for a number of alloy structures. The polyhedra are modified in the sense that the bonding planes are spaced along bond lines so as to reflect the relative metallic radii of the constituent atoms involved. The detailed positioning of these planes does not affect the results reported here. Some features of Voronoi polyhedra are discussed [4] briefly elsewhere in

these proceedings and one other factor must be noted here. Sometimes very small faces occur with areas of zero to two percent of the total area of the polyhedra and by their very presence affect the apparent edge count, and hence the ligand character, of other faces. These small faces are presumed to be relatively unimportant chemically and magnetically and any contributions they may make to the edge counts of other faces is neglected in the considerations below. Transition-metal sites which are not explicitly mentioned, but which occur in the structures discussed below, have (once the small facets are accounted for) (0,0,12) polyhedra [5].

One group of transition metal-rare earth hard magnets include (or are otherwise closely related to) the hexagonal Laves and the CaCu_5 structures. While the Laves phase has no transition metal sites which have major ligand lines, the Fe(c) site in $\text{Nd}_2\text{Fe}_{17}$ and the Fe(j₂) site in $\text{Nd}_2\text{Fe}_{14}\text{B}$ are (0,0,12,2): in the former Fe has a major ligand to a Nd and to another Fe(c), while in $\text{Nd}_2\text{Fe}_{14}\text{B}$ the Fe has [6,7] a major ligand to a Nd(1) and a Nd(2). In other words, unlike Frank-Kasper phases, these structures allow the smaller Fe atoms to have ligand lines to their neighbors, and these ligands involve the rare earths. As noted by Herbst et al

[6], these sites have the largest magnetic 3d moments in their respective structures and are cognates of one another. Now, the strong exchange coupling in such hard magnets is between transition metal moments and not between transition metal and rare-earth 4f moment. If the major ligand lines are to be important, they must relate to 3d-3d coupling via "superexchange" involving (i) the s-d bands of the intervening rare earths and (ii) the 6-fold sets of neighbors along the ligand lines. Since this view is somewhat different from the more traditional idea of magnetism in metals involving nets of near-neighbor direct exchange-coupled 3d moments, some experimental verification should be sought, perhaps by judicious substitutional alloying.

The two-fold CoI site of SmCo_5 has a (0,3,6,3) polyhedron, i.e., there are minor (4-fold) ligands (i.e., positive disclinations) between coplanar atoms as well as major ligands to the coplanar Sm atoms. There tend to be but small differences between the moments at the transition metal I with its (0,3,6,3) and the II with its (0,0,12) sites in this structure. Perhaps the presence of positive as well as negative disclinations on the CoI site prevent the development of full moments. This structure will need further study. For the most part, 3d magnetic ion sites with ligands have

(0,3,6,3), (0,3,6,4) and (0,0,12,2) polyhedra in the transition-metal rich -rare earth compounds. There is the suggestion that the tendency to form hard ferromagnets increases as a given structure has sites which traverse this sequence. That is, it is better to have (0,0,12,2) sites than either (0,3,6,4) or (0,3,6,3) and, in turn, these are better than (0,0,12). This issue is under further investigation.

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