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14. ABSTRACT Computational materials science is a comparatively new discipline that may forever alter the way in which materials are made and improved. This discipline seeks to use modeling and simulation to predict the properties of materials that have yet to be made. It is hoped that the ever-increasing power of computation can be harnessed to aid the materials designer and thereby accelerate the pace and reduce the cost of materials development. Because the objective of this new discipline is to aid in the design of materials, its advancement does not rely exclusively on increasingly sophisticated computational models. This advancement also requires the integration of these with traditional approaches to materials design, which make use of processing-structure-property relationships. It is argued here that the established descriptions of molecular structure and bonding can not be placed in the form of processing-structure-property relationships. Before quantum mechanical methods can be used in the discovery of such relationships, a new way to describe bonding is required. In this AFOSR funded program, such a description of the chemical bond was developed. It was shown, for specific phenomena, this new description could be used to construct processing-structure-property relationships. As these relationships were studied, it became evident that intrinsic mechanical properties are controlled by well-characterized boundaries that separate one bond from another. An understanding of how these boundaries move in response to an applied strain is necessary before it will be possible to uncover generalized relationships between the quantum mechanically determined charge density and mechanical properties.

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I. Structure in Materials Design

Materials design proceeds through the manipulation of structure. Cyril Stanley Smith [1] described materials structure in terms of a hierarchy with each of its levels characterized by a different length scale. In practice, it has been found that structures at one length scale often independently control properties. The nature of this control is expressed in the form of structure-property relationships, providing materials designers with the ability to alter properties through the independent manipulation of the individual elements of the structural hierarchy. The manipulation of structure is accomplished through the application of various chemical, thermal, and mechanical perturbations, described generally as processes. Thus, there are also relationships between processing and structure. Olson [2] has described how processing, structure, and properties constitute three of the four crucial elements in materials science, with the forth being performance. Though there is no agreement as to how these elements are connected, Olson argues that the linear structure

$$PROCESSING- > STRUCTURE- > PROPERTIES$$

has proved useful in the systems approach to materials design. For a materials designer the concept of structure is more profound than that associated with the simple arrangement of a material's constituent parts. Structure is not seen as isolated from the two critical elements bounding it: processing and properties. Structure both implies that properties originate from this structure and that it can be manipulated to produce changes in these properties. Structure is an inseparable element of a processing-structure-property relationship.

Atomic scale structure and properties

For the better part of this century, it has been recognized that whether a material fails in a ductile or brittle manner is governed by the atom-atom interactions at the tip of an atomically sharp crack [3-5]. As design tolerances are less severe when using ductile materials, alloy developers frequently look to promote more ductile behavior. However, because the relevant level of structure (atomic scale) is experimentally inaccessible, there

are no structure property-relationships to guide the alloy designer in this pursuit. In the absence of appropriate relationships, facets of this development proceed empirically, slowing the pace and increasing the cost of alloy design.

The recognition that quantum mechanical modeling could be used to investigate the relationships between atom-atom interactions and ductile or brittle failure provided the impetus to employ these approaches in the search for structure-property relationships. However, the structure needed to describe these atom-atom interactions is not given simply in terms of atomic positions. It also depends on the nature of the bonds linking atoms. The bonds and atoms together constitute a molecule's structure. The existence of relationships between properties and molecular structure is assumed in what Bader [6] calls the molecular structure hypothesis, asserting that all molecular properties derive from this linked set of atoms.

Typically, one thinks of structure-property relationships as expressing the control structure has on properties. However, Cohen [7] has argued that structure can also be viewed as being controlled by properties, wherein an element of structure is associated with the property that needs to be understood and controlled, a principle termed 'reciprocity'. As explained by Cohen, the history of science is replete with examples of reciprocity.

The reciprocity principle figures prominently in the evolution of our descriptions of molecular- structure. Known to every first year chemistry student is the common classification of bonds as ionic, covalent, Van der Waals, or metallic; a classification scheme that grew exclusively from reciprocity relations. It was Arrhenius' (ca. 1885) need to explain the property of electrical conductivity on the part of some solutions that gave rise to the ion and the description of a crystal as ionic. Lewis (ca. 1916) originated the covalent bond as a way to explain the existence of binding forces in nonionic molecules. The need to explain the formation of condensed phases by molecules whose atoms possessed a full octet of electrons led to the Van der Waals bond (ca. 1922). The metallic bond (ca. 1925) grew from the need to explain the differences in conductivity between nonionic solids. All of these representations of the bond were devised before the discovery of quantum mechanics.

In some cases, they even violate its laws. However, they were so effective in explaining the chemical phenomena of interest in the first half of the 20th century, that they became the principal descriptors of molecular-structure.

Beginning with the calculations of Eberhart, Johnson, Messmer, and Briant in 1981 [8], and numerous subsequent investigations [9-34] the methods of computational quantum mechanics have been employed in the examination of alloy failure. The purpose of all these investigations was to search for features of the charge density that could be associated with ductile or brittle failure. While the results of these calculations have explained the origins of mechanical response in some specific systems, (e.g. [9, 21]) no general structure- property relationships have emerged.

For the most part, quantum mechanical investigations of materials failure begin with a thermodynamic rational for ductile versus brittle behavior. For example, efforts to uncover the atomic origins of embrittlement in steel [11, 21, 22] have made use of the Rice-Wang [35] criterion for brittle failure. Using this criterion, an element's embrittling potency is determined by the difference in its segregation energy to a grain-boundary and free surface, with larger values indicating a more potent embrittling element. With density functional methods, it is possible to calculate this energy difference with sufficient accuracy to account for the observed trends in embrittling potency of common segregants. In reviewing these calculations, Olson has stressed [2] that only the most advanced calculations, employing non-local corrections to the density functional, can be used to uncover the thermodynamic basis of materials failure. Once an energy difference has been determined, relationships between the calculated molecular structure and ductile or brittle behavior are sought. Often, the structure of the charge density is described using the traditional (reciprocity derived) terminology of molecular structure, in other words as ionic, covalent, or metallic bonding etc. For example, Hong and Freeman [24] have suggested that brittle failure in NiAl is the result of directional covalent bonds. Yoo and Fu [25], on the other hand, have suggested reduced directionality of the same bonds is responsible for NiAl's failure properties. Shultz and Davenport [23] concluded, after a systematic survey of all bond types, that there were no apparent relationships between molecular structure and the

failure properties of FeAl, CoAl and NiAl.

In all of these investigations the importance of highly accurate calculations, which made no approximations as to the shape of the potential and often included non-local corrections to the density functional, was stressed. However, these analyses of the charge density were qualitative. Additionally, all of this interpretation is done without reference to the fact that the description of the electronic structure of a solid as ionic, covalent or metallic are examples of the principle of reciprocity at work. These representations of structure are a consequence of the need to explain properties of materials unrelated to mechanical behavior. It is unreasonable to expect that the very small changes in energy that have been found responsible for transforming a material from ductile to brittle will appear as large changes in the charge density, which can be described qualitatively. It is equally unreasonable to expect that these changes can then be mapped onto reciprocity relationships developed to account for a material's conducting properties.

Before the advances achieved in quantum mechanical modeling will be useful in materials design, a new way to describe the structure of the charge density must be found. There are three constraints placed on any such description. First, it must be quantifiable, with a clear correspondence between calculated energies and changes in the structure of the charge density. Second, the structure must be susceptible to predictable alteration. One must be able to predict how changes in chemistry are likely to change the structure. And third, one must demonstrate the existence of relationships between this structure and properties. In short, the quantum mechanically determined charge density must be incorporated into a processing-structure-property relationship. Over the last eighteen months of the existing two-year program, such a relationship has been proposed and shown, for some specific properties, to be useful as a tool for alloy design. In the following section, the accomplishments of the last eighteen months will be briefly reviewed.

II. A New Description of the Bond

Bader's theory of Atoms in Molecules (AIM) [6] provides the starting point to describe electronic structure. It is known from the Hohenberg-Kohn [36] theorem that all ground

state molecular properties are a consequence of a molecule or solid's charge density, a scalar field denoted here as $\rho(\mathbf{r})$. Bader noted $\rho(\mathbf{r})$ as a scalar field as a well-defined topology.

The topology of a scalar field is given in terms of its critical points, which are the zeroes of the gradient of this field. There are four kinds of critical points in a three dimensional space: a local minimum, a local maximum, and two kinds of saddle points. These critical points (cps) are denoted by an index, which is the number of positive curvatures minus the number of negative curvatures. For example, a minimum cp has positive curvature in three orthogonal directions, therefore it is called a (3, 3) cp. The first number is simply the number of dimensions of the space, and the second number is the net number of positive curvatures. A maximum is denoted by (3, -3), since all three curvatures are negative. A saddle point with two of the three curvatures negative is denoted (3, -1), while the other saddle point is a (3, 1) cp.

Through extensive studies of molecules, [6] Bader showed that it was possible to correlate topological properties of the charge density with elements of molecular structure and bonding. In particular, a "bond path" was shown to correlate with the ridge of maximum charge density connecting two nuclei, such that the density along this path is a maximum with respect to any neighboring path. The existence of such a ridge is guaranteed by the presence of a (3, -1) cp between bound nuclei. Because a (3, -1) cp is both a necessary and sufficient condition for the existence of a bond path, this critical point is sometimes referred to as a bond critical point (bcp). Other types of critical points have been correlated with other features of molecular structure. A (3, 1) cp is required at the center of ring structures like benzene. Accordingly, this critical point is designated a ring critical point (rcp). Cage structures are characterized by a single (3, 3) cp somewhere within the cage and are given the descriptive name of cage critical points (ccp). A maximum, a (3, -3) cp, is always found to coincide with an atomic nucleus and is called an atom critical point (acp).

Bader also showed there are regions within a molecule for which properties are well defined and additive, to give the corresponding values of the molecular properties. A

sufficient condition for delineating these regions is that they be bounded by a continuous surface of zero flux in the gradient of the charge density, here simply called zero flux surfaces. Every molecule or solid can be partitioned into volumes Ω_j such that each is bounded by such a surface, S, where $\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0$ for all $\mathbf{r}$ on S where $\mathbf{n}$ is the normal to S at $\mathbf{r}$. The value of an observable $\hat{A}$ over Ω is defined as,

$$\mathcal{A}(\Omega) \equiv \langle \hat{A} \rangle_{\Omega} = \int_{\Omega} d\tau \; \rho_{\mathcal{A}}(\mathbf{r})$$

where $\rho_{\mathcal{A}}(\mathbf{r})$ is the property density of $\hat{A}$, i.e.

$$\rho_{\mathcal{A}}(\mathbf{r}) = \left(\frac{N}{2}\right) \int d\tau' \{\psi^* \hat{A}\psi + (\hat{A}\psi)^* \psi\}.$$

Here N is the number of electrons in the system and τ' are the spin and space coordinates of $N-1$ of these. Only under the condition that the volumes are bounded by a zero flux surfaces is it found that the molecular value of the observable is given by a sum of its contributions from each Ω_j, in other words that

$$\langle \hat{A} \rangle = \sum_j \mathcal{A}(\Omega_j).$$

Bader observed that there is a unique partitioning of any molecule into volumes bounded by zero flux surfaces, such that each volume contains one atomic nucleus. These volumes are called atomic basins and are the quantum mechanical analogues of the atoms in molecules. We noted [38] that when the requirement that each volume contain an atomic nucleus is lifted there is an alternative partitioning of space into nonintersecting volumes bounded by zero flux surfaces. This partitioning gives rise to what we called irreducible or tetrahedral bundles (as they are formed from the bundling together of gradient paths). Each of these is homeomorphic to a tetrahedron with its four vertices coincident with, a ring, a bond, a cage, and an atom critical point. These bundles can be packed variously to give rise to the charge density topology of any solid. No polyhedron, having a fewer number of vertices can be packed to fill three-dimensional space. It is in this sense that this bundle is irreducible.

A tetrahedral bundle is found by first identifying mutually adjacent bond, cage, ring and atom critical points. Two critical points are adjacent if joined by a gradient path, and three critical points are mutually adjacent if there is a closed 3-cycle of gradient paths connecting them. Thus four mutually adjacent cps lie at the vertices of a tetrahedron. The edges of this tetrahedron are defined to be the gradient paths of minimal length joining the adjacent cps. The faces of the tetrahedron are defined to be the gradient surfaces of minimal area containing the tetrahedral edges. These surfaces are not necessarily planar.

By construction, the irreducible-bundle is bounded by a surface of zero flux and thus characterized by well-defined properties. In addition, all molecular structures can be seen to arise in a natural manner from the union of these irreducible-bundles. The union of irreducible-bundles sharing the same maximum produces atomic basins. Now consider the union of irreducible-bundles sharing the same bond critical point. This is called a bond-bundle. The cps on the surface of a bond-bundle are homeomorphic to the vertices of a polyhedron, with two maxima, n ring and n cage points and no bond points. A single bond path, connecting the two nuclei, must be contained within a bond- bundle. Thus the bond-bundles of a solid define a set of space filling, non-overlapping polyhedra bounded by zero flux surfaces, each containing a single bond critical point and bond path. As such, the properties of the molecule can be expressed as a sum over the corresponding bond properties. Thus, the bond-bundles are the quantum mechanically well defined objects associated with bonds.

With the structure of atoms and bonds defined, the existence of relationships between electronic structure and properties can be found. As an example, consider the transition metal aluminides TmAl where Tm is one of the first-row transition metals: Cr, Mn, Fe, Co, or Ni. Of these, only CrAl, does not form the ordered B2 structure (Figure 1), rather it is disordered and is body centered cubic (bcc). Further, there is a variation of the failure properties of these alloys with CoAl being the most brittle and decreasing through the series: CoAl > NiAl > FeAl > MnAl > CrAl. Comparisons of the charge density, as determined through quantum mechanical calculations, indicate these variations in properties can be attributed to differences in the structure of the bond-bundles.

Without a rigorous description of the chemical bond, atoms are often assumed to be bound based on their interatomic spacing. In the case of the B2, and other structures with the same atomic packing, e.g. bcc, there is only a 14% difference in the distance between first and second neighbor atoms. Some have suggested that this is indicative of second neighbor bonding and attempts have been made to rationalize the properties of these alloys in terms of the relative amounts of first and second neighbor bonding. For a general XY B2 alloy each X (Y) atom has eight Y (X) nearest neighbor and six X (Y) second nearest neighbor atoms. Giving three possible types of bonds in an XY B2 alloy: X-to-Y nearest neighbor bonds, and X-to-X as well as Y-to-Y second neighbor bonds. Previous calculations [37] looking only at bond paths in a much larger set of alloys, found that a stable B2 structure is characterized by nearest neighbor bonds and one set of second neighbor bonds, Figure 1. Using the full potential linear augmented Slater-type orbital method (LASTO) to determine the charge density of each of the five transition metal aluminides, the same bonding was found to characterize these. CrAl, the only alloy which does not form a stable B2 structure, showed only first neighbor bond paths connecting Cr to Al atoms. Despite the fact that the B2 structure was imposed on this alloy, no second neighbor bond paths were found. In contrast, all other aluminides show both first and second neighbor bond paths, where the second neighbor bond paths join transition metal atoms.

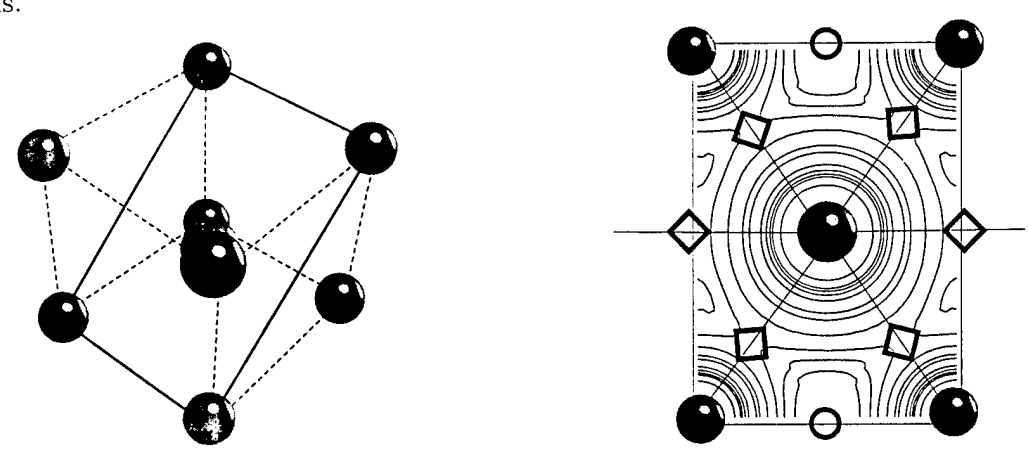

Figure 1. Left) The crystal structure of the B2 transition-metal aluminides. Here the transition-metal atom is shown as red while the aluminum atom is shown as blue. Right) The charge density in a (110) plane. The critical points are marked by type. A ◇ denotes the locations of bond critical points and a ○ marks the location of cage critical points.

The lines denote bond paths of two types: aluminum to transition- metal first neighbor bonds, and transition-metal to transition-metal second neighbor bonds.

Turning to the bond-bundles, the minimal gradient surfaces forming the boundaries between first and second neighbor bond-bundles are shown in Figures 2 and 3. Figure 3A shows half of the bond- bundle connecting second neighbor transition metal atoms; its complement is a mirror image. The variation of the bond-bundles through the series: CrAl, MnAl, FeAl, CoAl, and NiAl can be seen clearly in the cross section of these bond-bundles in an all aluminum (100) crystallographic plane, Figure 3B. This cross sectional area, which is directly related to the volume of the second neighbor bond-bundle, decreases through the series CoAl > NiAl > FeAl > MnAl > CrAl, disappearing at CrAl.

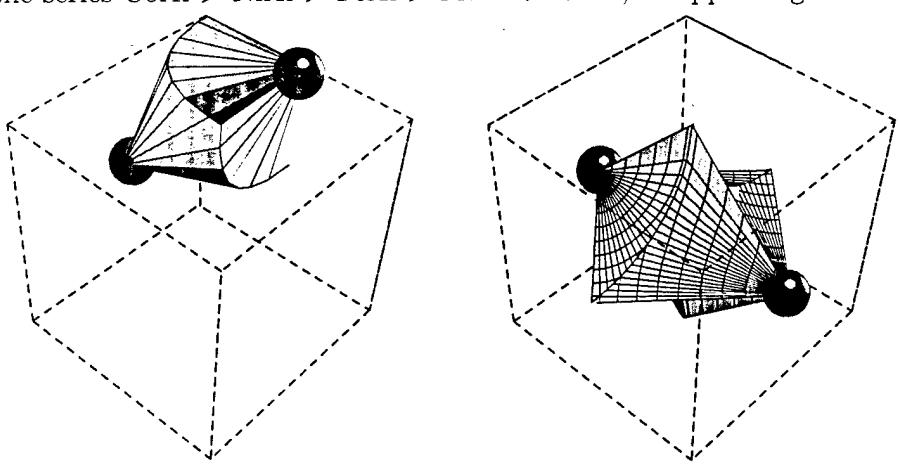

Figure 2. Left) The aluminum to transition-metal first neighbor bond-bundle. Right) Transition-metal to transition-metal second neighbor bond-bundle.

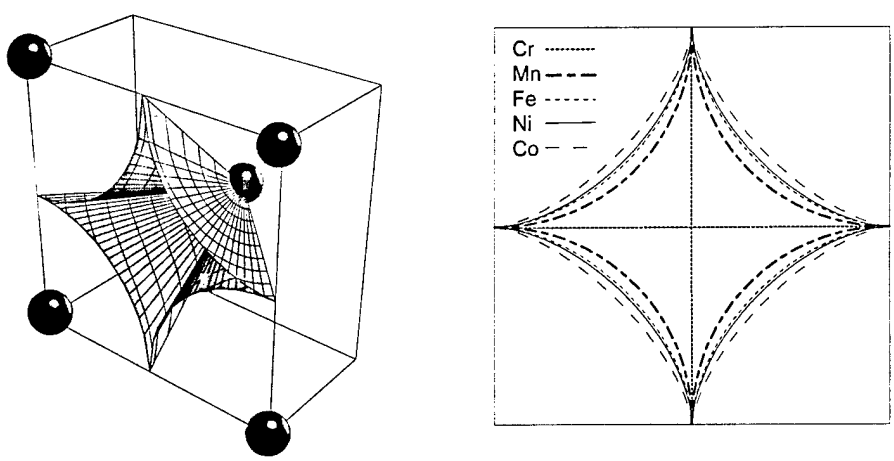

Figure 3. Left) Half of the second neighbor bond-bundle showing its intersection in an all aluminum atom (100) plane. The intersection cross-section is proportional to the volume

of this bond-bundle. CoAl shows the largest second neighbor bond-bundle while CrAl shows no second neighbor bond-bundle.

The zero flux property of the surfaces bounding the bond-bundle can now be exploited to get quantitative information regarding the relative energies of the first and second neighbor bonds. Bader [6] has shown that the virial theorem is satisfied for any volume Ω bounded by a zero flux surface. Thus, in a system where there are no external forces acting on the nucleons and the internal forces have vanished, i.e. the molecular energy is stationary,

$$2T(\Omega) = -V(\Omega)$$

where $T(\Omega)$ is the total kinetic energy of the electrons in Ω and $V(\Omega)$ is the total potential energy of Ω. Each region Ω can be assigned an energy $E(\Omega)$ such that

$$E(\Omega) = T(\Omega) + V(\Omega) = \frac{1}{2}V(\Omega).$$

Consequently, the total bond energy can be determined, to an additive constant, by integrating the potential over the appropriate bond-bundle. Determining the difference in energy density between first and second neighbor bonds may eliminate the constant. In units of micro-hartrees per cubic bohr the calculated variation in this energy density difference across the series MnAl, FeAl, CoAl, NiAl is 1.34, 1.12, 0.86 and 1.08 respectively. Not surprisingly, as the energy density difference between first and second neighbor bonds is minimized (at CoAl), the volume of the unit cell involved in second neighbor bonding increases. Thus CoAl, with the smallest energy density difference and the largest second neighbor volume, has the largest component of its total energy derived from second neighbor bonding. At the other extreme is MnAl with the smallest component of its total energy derived from second neighbor bonding. As a percent of total energy derived from second neighbor bonding CoAl > NiAl > FeAl > MnAl > CrAl. This trend is identical to the trend in failure properties of these alloys. There is a relationship between the relative energy invested in first and second neighbor bonding and the failure properties of the modeled aluminides.

Once a relationship between a structure, in this case bond-bundles, and properties is

established, one- electron theory and coordination chemistry provide the formalism to alter structure i.e. the processing component of a processing-structure-property relationship. As these theories are well established their application will be only briefly reviewed. In the case of the B2 structure, the d-orbitals on the transition metal atoms are of two types, those that contribute density to the nearest neighbor bond- bundles and those that contribute density to the second neighbor bond-bundles. The d_{xy}, d_{xz}, and d_{yz}- orbitals are of the first type, while the $d_{x^2-y^2}$, and d_{z^2}-orbitals are of the second type. By altering local structure, the relative populations of these two types of orbitals can be modified in a predictable way, changing the relative volume of first and second neighbor bond-bundles and the properties that derive from their relative volumes. This form of analysis suggests the substitution of Fe or Mn for Ni in NiAl will increase intrinsic ductility, as has been observed.

With the ability to partition the charge density into regions that can be associated with individual bonds, it becomes possible to analyze a mechanical distortion in terms of bond forming and bond breaking contributions. This gives rise to structure-property relationships that can be used to alter properties without first calculating a bond energy. For example, we have used LMTO methods [39] to follow the molecular structure of three fcc metals through a rigid shear, creating stacking faults. The metals studied were iridium, aluminum, and silver. In the formation of a stacking fault, some bonds are broken while others are formed. The stacking fault energy is simply the energy necessary to break bonds offset by the energy realized in bond formation. In this investigation, it was found that the unstable stacking fault (the configuration at the point of maximum energy in the shear) coincided with the vanishing of an existing bond-bundle and the formation of a new one. Further, the stacking fault energy correlated well with the volume difference between the old and new bond- bundles. By way of illustration, the bond-bundles of silver, in both the fcc and stacking fault configurations, were nearly indistinguishable. Indicating a small stacking fault energy, as is observed. In the case of aluminum, the bond-bundles of the stacking fault are smaller than those of the fcc crystal. Consistent with the observed high stacking fault energy of aluminum. As in the case of the B2 aluminides, once a structure-property relationship is uncovered, it proves possible to suggest alloying elements that

would alter structure, and therefore, properties. In this case, the stacking fault energy of aluminum could be lowered by promoting bond formation and withdrawing charge density from one of the irreducible-bundles giving rise to aluminum's molecular structure. Magnesium atoms would have this effect, and it is known that small additions of Mg do indeed lower the stacking fault energy of aluminum.

For both of the investigations reviewed above, the changes in the charge density were so subtle that they would be undetectable if not analyzed in terms of the changes produced in the bond-bundles. By way of illustration, though the change in the relative volumes of first to second neighbor bond- bundles is evident in Figure 3, this is only a consequence of the fact that gradient surfaces have been identified. Without this identification, the changes occurring at the surface of the bond-bundles are far from obvious. It is at the interface between irreducible-bundles where the mechanical properties of an alloy are ultimately mediated. Here, strain acting on these surfaces causes them to move such that some irreducible-bundles grow at the expense of others. The structure-property relationships sought here will relate the structure of an irreducible-bundle to its behavior under an applied strain.

There is some initial evidence suggesting the form these structure-property relationships may take. This initial evidence comes from studies of irreducible-bundles in fcc transition metals. As is well known, the fcc structure is characterized by tetrahedral and octahedral holes. In terms of the charge density, these holes can be constructed through the union of irreducible-bundles sharing a common ccp. Conventionally in the fcc structure, every octahedral hole is shown as sharing planar triangular faces with tetrahedral holes. However, when the irreducible-bundles are constructed that form these holes, it is found that the triangular faces marking the boundaries between octahedral and tetrahedral holes are not necessarily planar. Faces that are not planar require one of the holes, octahedral or tetrahedral, to be a convex polyhedron while the other is a concave polyhedron. In copper the octahedral hole is convex (the octahedral faces are bowed out, away from the octahedral center), in aluminum and iridium the octahedral hole is concave, and in silver the octahedral faces are nearly planar. This same characteristic, i.e. a curved face

bounding irreducible-bundles, is shown in Figures 2 and 3. There, the surfaces separating first and second neighbor bond-bundles are curved, making the second neighbor bond-bundle a concave polyhedron. The susceptibility for one irreducible-bundle to grow at the expense of another is correlated with the curvature of the face separating these bundles. Never has there been a suggestion that there are relationships between the structure of well-characterized boundaries within the charge density and mechanical properties. An understanding of these relationships will provide the basis for the design of alloys with desired intrinsic mechanical properties.

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