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Appendix A

"Theoretical Evidence for Specificity of Metal-Metalloid Interactions in Fe–Ni–P–B Glasses", R. P. Messmer, Proceedings of "Conference on Metallic Glasses: Science and Technology, 1980", Budapest, Hungary, in press.

DISCLAIMER

Proceedings of "Conference on Metallic Glasses: Science and Technology, 1980", Budapest, Hungary, in press.

THEORETICAL EVIDENCE FOR SPECIFICITY OF METAL-METALLOID INTERACTIONS IN FE-NI-P-B GLASSES

R. P. Messmer

General Electric Corporate Research and Development
Schenectady, New York 12301, U.S.A.

ABSTRACT

Detailed quantum mechanical calculations are carried out on clusters of atoms which simulate possible local environments in amorphous metal alloys. The clusters used are based on simple Bernal polyhedra and distortions of these polyhedra. The materials being studied are the (Fe, Ni, B, P) alloys. The simplest Bernal polydehron, the tetrahedron, is considered as a first model for the local environment in $Fe_{40}Ni_{40}B_{20}$ and $Fe_{40}Ni_{40}P_{20}$ alloys.

INTRODUCTION

For the case of metal-metalloid amorphous alloys there appears to be a general consensus that the Bernal polyhedra offer a useful first approximation to the local atomic arrangement. In the alloys of interest here, it will be assumed that a B or P atom resides in the interstitial hole of a Bernal polyhedron. This seems reasonable as the size of these atoms is considerably smaller than a transition metal atom and further the polyhedron might relax to better accommodate such a metalloid atom. In this paper only the smallest Bernal polyhedron - the tetrahedron will be considered in any detail, even though other polyhedra may constitute more appropriate local environments for a metalloid atom. It is clear that a variety of local environments must be explored in order to arrive at a perspective which one could consider to be general. However, the reason for the initial focus on the tetrahedron is simply that a number of important conceptual and computational questions can be addressed with a minimum of computational time and expense. The most important question for this work, is whether there is significant bonding between metalloid and metal atoms. And if there is, to elucidate the nature of the bonding.

It should be mentioned that previous work which has employed molecular orbital electronic structure calculations in conjunction

with clusters of atoms representing a local region of a solid has provided unique insight into a number of problems; these include defects in semiconductors [1], chemisorption [2], magnetic impurities in metals [3] and impurities at grain boundaries of metals [4].

RESULTS FOR TETRAHEDRAL CLUSTERS

In *Fig. 1*, the geometry of the cluster is shown together with the coordinate system which will be used to discuss the results. The Ni atoms are contained in the yz plane and the Fe atoms in the xz plane. The electronic structure calculations employed the self-consistent-field-Xα-scattered wave (SCF-Xα-SW) method which has been described in detail in the literature [5] and which has been previously applied to a variety of problems involving metal clusters [2-6]. The present calculations have been carried out within the spin-polarized framework in order to account for the magnetic effects of Fe-Ni clusters. If one choses a metal-metal distance for the clusters appropriate to bulk Ni or Fe, the metal-metalloid distance of 1.53Å is too short. Hence the cluster was expanded to give a metal-metalloid distance of 2.13Å, which is more consistent with known distances in the crystalline compounds Fe_3P and Ni_3B [7].

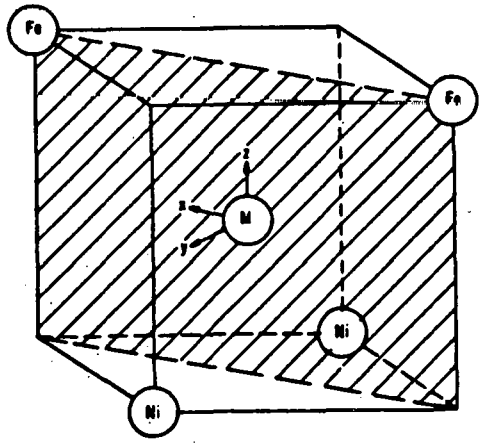

Fig. 1 Geometry of Clusters

From the results of the calculations [8], it is found that there are significant bonding interactions between the p-orbitals of B and P atoms and the atomic orbitals of the transition metal atoms. One interesting question which comes to mind with regard to analyzing these results is whether there is a preferential interaction between a given metalloid atom and the Fe or Ni atoms

in the cluster. If such perferential interactions do occur they would have a profound effect on the conceptual framework with which we view metalloid-transition metal glasses. For TM-TM'-M systems, one could no longer view the metalloid atoms as simple filling in the Bernal holes of a DRPHS structure of metal atoms. Rather, one would have to admit to the possibility of a local atomic scale chemistry arising from such electronic interactions.

In order to ascertain whether there are specific interactions between metal atoms and metalloid atoms, an analysis of bonding charge densities between the metalloid atom and the metal atoms should be particularly useful. As there are relatively few molecular orbitals which describe the metal-metalloid interaction, it is convenient to consider a partial charge density or bonding charge density where one only sums over those orbitals which contain metalloid (M) character. If this latter charge density is denoted as ρ_B for the case of the Ni_2Fe_2B cluster and if this charge density is plotted in the yz plane *(Fig. 1)*, which will be denoted as ρ_B^{yz}, it should show the metalloid bonding to the Ni atoms. On the other hand, if it is plotted in the xz-plane the charge density ρ_B^{xz} should show the metalloid bonding to the Fe atoms. In order to see if there is a preferential interaction, a difference density, $\Delta\rho_B$ can be obtained by aligning the metal atoms from the two planes such that they coincide. Thus $\Delta\rho_B$ is defined as $\Delta\rho_B = \rho_B^{yz} - \rho_B^{xz}$, once the metal atoms have been properly aligned. If there is a preferential interaction between the B atom and Ni atoms, positive contour lines of $\Delta\rho_B$ should surround the B atom as ρ_B^{yz} is in the Ni_2B plane, whereas negative contour lines of $\Delta\rho_B$ should surround the B atom if the preferential interaction is between B and the Fe atoms (ρ_B^{xz} is in the Fe_2B plane). A contour plot of $\Delta\rho_B$ for the Ni_2Fe_2B cluster is shown in *Fig. 2*. The contours around the B atom are positive indicating a preferential B-Ni interaction.

A similar analysis for the Ni_2Fe_2P cluster shows a preferential P-Fe interaction. Thus we conclude from these preliminary studies on small clusters that for these types of metallic glasses there are very likely preferential bonding interactions between the pairs B-Ni and P-Fe.

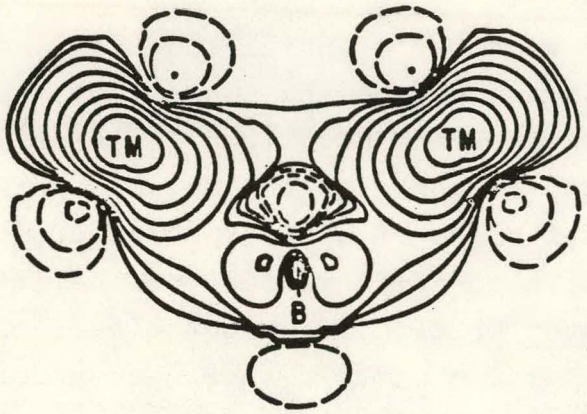

Fig. 2 Contour plot of $\Delta\rho_B$ for the Ni_2Fe_2B cluster. Solid lines and dashed lines represent positive and negative charge density respectively.

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