PHYSICAL REVIEW B VOLUME 37, NUMBER 14 15 MAY 1988-I

Environmentally specific mechanical properties: Beyond atomic parameters

M. E. Eberhart* and D. D. Vvedensky
The Blackett Laboratory, Imperial College, London SW7 2BZ, United Kingdom

(Received 16 November 1987)

Representative wave functions of Cu, Ir_3Cr, and Zr_3Al as determined from multiple-scattering $X\alpha$ cluster calculations are compared. While atomic parameters, specifically s-orbital electronegativities, predict an isotropic charge density for Ir_3Cr and an anisotropic charge density for Zr_3Al, quite different characteristics are observed. This is rationalized in terms of an effective s-orbital electronegativity which is sensitive to the local atomic environment. The actual charge density that results from these effective electronegativities correlates well with the observed mechanical properties, with the most isotropic charge density corresponding to the most ductile material.

New materials development is increasingly controlled at a scale which is experimentally inaccessible. The production of interfaces with particular thermal, electrical, or mechanical properties serve as examples where macroscopic behavior is strongly influenced by atomic-scale interactions near the interface. As the experimental techniques for studying these interactions are limited, researchers are making increasing use of first-principles quantum-mechanical calculations as tools in the investigation of such interactions. In particular, the study of grain boundary mechanical properties has recently been the subject of intense computational investigation.[1-9]

While most of the first-principles investigations of mechanical properties have been directed toward an understanding of the electronic factors that influence environmentally induced intergranular failure,[1-6] recent studies have focused on the incipient event leading to fracture.[6-9] In those studies, an approach was developed for predicting the tendency toward brittle behavior in polycrystalline materials by focusing upon the ease with which isotropic bonds can be formed in response to the bond misorientation found near typical grain boundaries and crack tips. It has been argued that brittle materials are characterized by a less isotropic charge density than are ductile materials.[7] It was further conjectured that the relative s-orbital electronegativities of alloy constituents in ordered alloys should provide a first approximation to total isotropic charge density.[7,8] In A_xB alloys, elements showing similar s-orbital electronegativities will tend to be ductile, while elements with dissimilar s-orbital electronegativities will tend to be brittle. This conjecture was well supported by property maps,[8] of the type shown in Fig. 1, in which ordered alloys would partition into ductile and brittle regions when A-vs-B *atomic* s-orbital electronegativities were plotted.

Though the general trends of the property maps are in good agreement with experimental observation, our attention has been directed to several ill-behaved points. Of relevance to this paper are the points corresponding to Ir_3Cr and Zr_3Al. Ir_3Cr is predicted to be ductile while it has been found to be quite brittle,[10] and Zr_3Al has been reported to be ductile[11] though the property maps predict brittle behavior. The apparent failure of the property maps is almost certainly due to the use of *atomic* orbital electronegativities rather than the effective orbital energy of the atoms in the alloy environment. As has been discussed elsewhere,[7] orbital energy values are a sensitive function of environment and one must identify the effective atomic states in the compound in order to account for possible charge transfer and rehybridization. Thus it was expected that more accurate predictions of mechanical properties would require a knowledge of the extent of isotropic charge density resulting from the environmentally induced orbital energies.

In this paper we report the results of multiple-scattering $X\alpha$ (MS-$X\alpha$) cluster calculations[12] on models of the local environment of crystalline Ir_3Cr and Zr_3Al. We show that while predictions regarding mechanical behavior based on atomic orbital energy values are incorrect, predictions based on calculated isotropic bonding character are in accordance with observation. It is further shown that the net isotropic bonding character provides a basis for comparison of mechanical properties between metals and alloys of different compositions. Finally, we discuss the limitations of all methods which use fixed atomic values as parameters in the quantification of material properties.

The net isotropic charge character for Ir_3Cr and Zr_3Al was calculated using the MS-$X\alpha$ formalism.[12] In addition, the charge density for pure copper was also calculated in order to provide a standard from which to compare the calculated charge density for the alloys. For each of these calculations a 19-atom cubo-octahedral cluster was used, in which the central atom (Cr, Al, or Cu) is surrounded by 12 near-neighbor atoms (Ir, Zr, or Cu) and six second-neighbor atoms (Cr, Al, or Cu). The interatomic distances used were those of the appropriate bulk metal or alloy. Additionally, the calculation of the Ir_3Cr system was spin-polarized, consistent with the observed ferrimagnetic behavior of this alloy system.[10] Interestingly, the spin polarization produced only minor alterations in the net isotropic bonding character.

Though the net isotropic charge density results from all orbitals of the manifold, the limitations of space require that specific, representative wave functions be used to illustrate the differences in calculated charge density corre-

© 1988 The American Physical Society

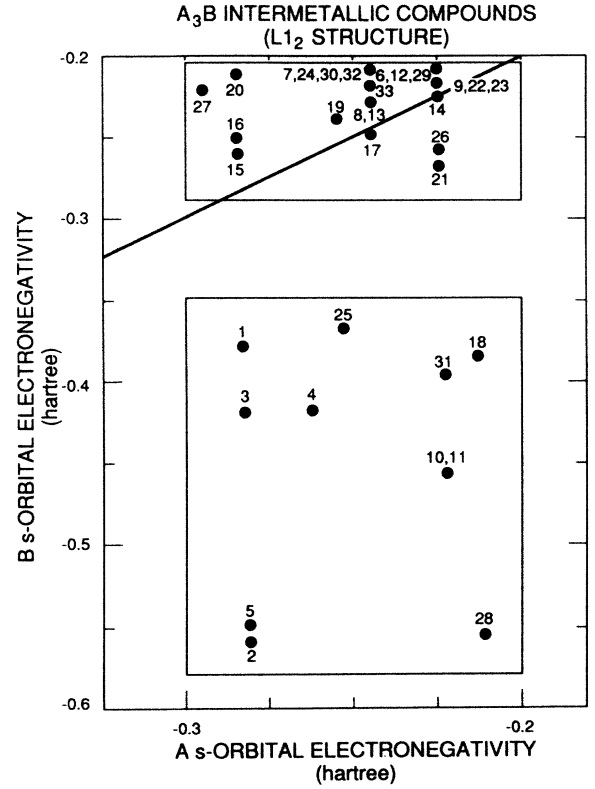

FIG. 1. The s-orbital electronegativity (in hartrees, 1 hartree = 27.2 eV) of constituent A plotted against that of B for 33 A_3B intermetallic compounds with the $L1_2$ structure. Those points with similar electronegativities are predicted to be ductile while those with dissimilar values are predicted to be brittle. 1, Ni_3Al; 2, Ni_3Si; 3, Ni_3Ga; 4, Fe_3Ga; 5, Ni_3Ge; 6, Cr_3Pt; 7, Ir_3Ta; 8, Ir_3Ti; 9, Pt_3Ti; 10, Pt_3Pb; 11, Pb_3Pb; 12, Rb_3Ta; 13, Ir_3Va; 14, Rh_3V; 15, Ni_3Fe; 16, Ni_3Fe; 17, Cu_3Au; 18, Zr_3Al; 19, Au_3Cu; 20, Zn_3Nb; 21, Pt_3Co; 22, Pd_3Cr; 23, Pt_3Cr; 24, Cu_3Pt; 25, Mg_3In; 26, Pd_3Fe; 27, Ni_3Pt; 28, Nb_3Si; 29, Rh_3Nb; 30, Ir_3Nb; 31, Pt_3Al; 32, Cu_3Pd; 33, Ir_3Cr.

sponding to brittle or ductile materials. The $1a_{1g}$ orbital of copper is shown in Fig. 2. This is typical of ductile metals, with all first-row transition metals showing very similar charge distributions. Of particular interest is the partial-wave decomposition for this molecular orbital which is described in Table I, while the charge distribution for this orbital is shown in Table II. The result is the very diffuse, isotropic orbital of Fig. 2(a). This should be compared to the $1a_{1g}$ orbitals of Zr_3Al and Ir_3Cr shown in Figs. 2(b) and 2(c). As determined by inspection of Tables I and II, the $1a_{1g}$ of Zr_3Al is less isotropic than that of Cu with significant d hybridization. The $1a_{1g}$ of Ir_3Cr is less isotropic still. The d hybridization on the Ir atoms is dramatic with almost 80% of the partial-wave component being of d character. Thus, the $1a_{1g}$ of Ir_3Cr is highly directional, being more d-σ than s-σ in character.

This strong d-σ character of the $1a_{1g}$ orbital is characteristic of strong directional bonding and is also seen in the results of cluster calculations on pure Ir metal and recent work on pure W. We conclude, from inspection of

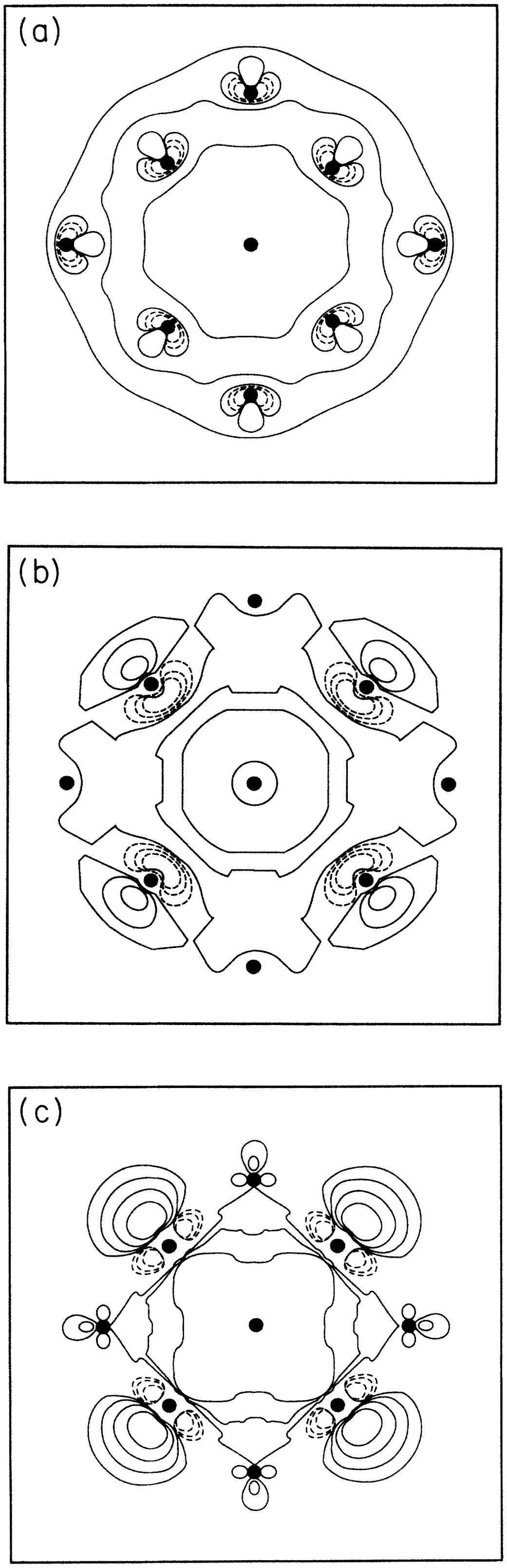

FIG. 2. (a) The $1a_{1g}$ orbital of a Cu_{19} cluster. The contour values are 0.001, 0.003, 0.009, 0.027, and 0.081. Positive and negative values of the wave function are shown by solid and broken lines, respectively. (b) is the same as (a) for Zr_3Al. (c) is the same as (a) for Ir_3Cr.

TABLE I. Partial-wave decomposition (%) for the central atom (A), the first coordination sphere ($A1$), and the second coordination sphere ($A2$).

	A			$A1$			$A2$		
	s	p	d	s	p	d	s	p	d
Cu	100	0	0	72	17	11	67	21	12
Zr$_3$Al	100	0	0	44	28	26	80	17	3
Ir$_3$Cr	100	0	0	12	9	78	32	16	53

TABLE II. Charge distribution (%) for the central atom (A), the first coordination sphere ($A1$), the second coordination sphere ($A2$), and the intersphere region (Int.).

	A	$A1$	$A2$	Int.
Cu	25	44	4	27
Zr$_3$Al	57	29	2	12
Ir$_3$Cr	17	69	0	14

the wave functions of Fig. 2, that Cu is characterized by the most isotropic bonding while Ir$_3$Cr is characterized by the least isotropic bonding. Zr$_3$Al falls somewhere in between, probably closer to Cu than Ir$_3$Cr. Thus, by utilizing our model of intrinsic mechanical behavior, we are able to conclude that intrinsically Cu is more ductile than Zr$_3$Al, which is more ductile than Ir$_3$Cr. We postulate that the net isotropic character of cluster charge density correlates with a measure of intrinsic ductility such as elongation to fracture, though many more calculations and comparisons of the type presented here will be required to firmly establish this correlation. Note that the isotropic character of the charge density need not be determined through cluster techniques, band calculations will also serve. We are currently using the recently developed layer-Korringa-Kohn-Rostoker technique to calculate charge densities and compare with cluster results. Initial results indicate that the same trends are observed.

The possibility that intrinsic ductility may correlate with isotropic charge distribution could be of tremendous importance to the alloy design industry. The ability to assess the effect of dilute ternary additions on the mechanical properties of alloys through simple quantum-mechanical modeling is a reasonable alternative to time consuming and costly empirical techniques.

The use of atomic *fixed*-parameter systems to describe physical and mechanical behavior of alloys is common. Hume-Rothery and Raynor rules[13] are based on such fixed quantities as atomic size, electron-to-atom ratio, and electronegativity. More recently Takasugi and Izumi[14] suggested that A-vs-B group numbers for A_3B alloys would predict intrinsic mechanical properties and, in fact, lead to plots remarkably similar to Fig. 1. Pettifor[15] makes use of empirically determined Mendeleev numbers to provide structural partitions of binary compounds for a variety of stoichiometries. It has been noted[8] that these structure maps also provide a ductile brittle partitioning identical to Fig. 1. However, unlike Mendeleev numbers and group numbers, which are meaningful only for isolated atoms, size, electron-to-atom ratios, and orbital electronegativities also have meaning within a particular chemical environment. Thus these quantities can be used to parametrize the chemistry of a molecule or solid. The difference in *effective* s-orbital electronegativity for Ir and Cr in the Ir$_3$Cr environment, as determined from the cluster calculations, is 0.055 hartrees while for Zr and Al in Zr$_3$Al it is 0.008 hartrees. This shift in relative orbital energies from the isolated atom to the atom in the alloy environment is a measure of the chemical interaction between elements A and B in a specified structure. Such a cross term cannot be determined from fixed atomic values such as group number, Mendeleev number, or atomic-orbital electronegativities. Any parametrization of solid-state properties must account for sensitivity to environmental modification.

This work was supported in part by a NATO travel grant and by a grant from AFWAL. One of us (M.E.E.) is grateful for the hospitality shown him while at Imperial College where this work was conducted. The authors are grateful to D. Pope and A. Taub for bringing the properties of the alloys discussed in this paper to their attention.

---

[*] Permanent address: Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.

[1] C. L. Briant and R. P. Messmer, Philos. Mag. B **42**, 569 (1980); R. P. Messmer and C. L. Briant, Acta. Metall. **30**, 457 (1983); **30**, 1811 (1982).

[2] W. Losch, Acta Metall. **27**, 1885 (1979).

[3] R. Haydock, J. Phys. C **14**, 3807 (1981).

[4] M. E. Eberhart, K. H. Johnson, and R. M. Latanision, Acta Metall. **32**, 955 (1984).

[5] G. S. Painter and F. W. Averill, Phys. Rev. Lett. **58**, 234 (1987).

[6] M. E. Eberhart, R. M. Latanision, and K. H. Johnson, Acta Metall. **33**, 1769 (1985).

[7] M. E. Eberhart and D. D. Vvedensky, Phys. Rev. Lett. **58**, 61 (1987).

[8] D. D. Vvedensky and M. E. Eberhart, Philos. Mag. Lett. **55**, 157 (1987).

[9] T. Takasugi and O. Izumi, Acta Metall. **33**, 1279 (1985).

[10] D. D. DiMicco and D. P. Pope, Met. Trans. **10A**, 1371 (1979).

[11] E. M. Schulson and J. A. Roy, Acta Metall. **26**, 29 (1978).

[12] K. H. Johnson and F. C. Smith, Jr., Phys. Rev. B **5**, 831 (1972).

[13] W. Hume-Rothery and G. V. Raynor, *The Structure of Metals and Alloys*, Institute of Metals Report Series (Institute of Metals, London, 1954).

[14] T. Takasugi and O. Izumi, Acta Metall. **33**, 1247 (1985).

[15] D. G. Pettifor, J. Phys. C **19**, 285 (1986).