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On the Catalytic Activity of Ni_3Ti*

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Based on the electronic structures of Ni_4 and Ni_3Ti clusters calculated by Fischer et *al., we* discuss the catalytic activities of Ni_3Ti and its interaction with atomic hydrogen.

BECAUSE the active sites in catalysts often consist of transition-metal clusters (or their intermetallic compound) of size less than 10 Å, the electronic structures of small metallic clusters are of considerable current interest. It is generally believed that the approximately half-filled *d*-band plays an important role in determining the catalytic properties of transition metals"[1]. However, to understand a specific catalytic activity of a small metallic or bimetallic cluster requires careful investigations on its electronic structure, both theoretical and experimental. In this communication, we discuss the catalytic activity of a Ni_3Ti cluster, particularly its interaction with atomic hydrogen. As there has been no experimental work done on this problem, we hope that this paper will generate some interest for experiments.

Our discussion is based upon the electronic-structure calculation by Fischer *et al.*, who used the SCF-$X\alpha$ method[2] for four-atom tetrahedral Ni and tetrahedral Ni-Ti containing three nickel atoms and one titanium atom. The spin-restricted molecular-orbitals for both Ni_4 and Ni_3Ti clusters, along with the SCF-$X\alpha$ 1s orbital energy for an isolated hydrogen atom[3], are displayed in Fig. 1. The levels are labelled according to the irreducible representation of T_d and C_{3v} point groups for Ni_4 and Ni_3Ti respectively. The highest occupied orbital is designated E_F, while the energies, occupancies, and the fractional principal partial-wave character for orbitals are listed in Table 1 for Ni_3Ti cluster.

The interaction of hydrogen atom with Ni and other transition-metal cluster has been studied by Messmer *et al.*[4] using SCF-$X\alpha$ method. The configuration chosen for study was a four-atom tetrahedral metal cluster containing atomic hydrogen at the tetrahedral interstitial site. The major results for Ni-H system can be summaried as follows:

1) The covalent bonding of atomic hydrogen at the cluster interstices with neighboring Ni is governed principally by two factors: the relative electronegativity of the symmetry conserving a_1 orbital near the bottom of the Ni, d-band with respect to that of the H 1s orbital, and the concomitant overlap of the corresponding orbitals.

2) The interaction of atomic hydrogen with Ni_4 cluster results in a hydrogen-metal bonding energy level of a_1 orbital symmetry, split off from the bottom of the d-band of Ni_4 cluster, accompanied by much smaller level shifts within the d-manifold.

3) The metallic 4s-like and 3d-like components are almost equally responsible for the bonding of hydrogen to the nickel aggregate.

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(2) T. E. Fischer, S. R. Keleman, K. P. Wang and K. H. Johnson, Phys. Rev. **B20**, 3124 (1979).
(3) J. C. Slater and K. H. Johnson, Phys. Rev., B5, 844 (1972).
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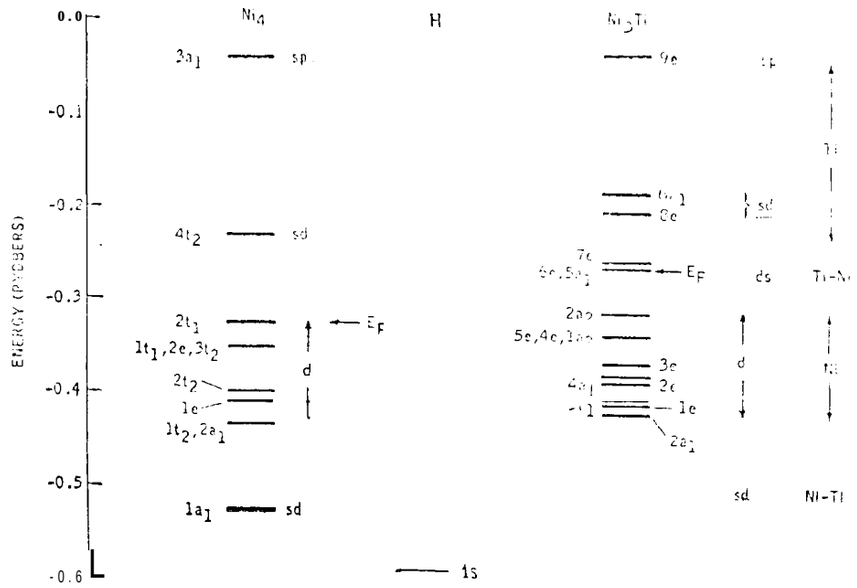

Fig. 1. Spin-restricted electronic energy levels for a tetrahedral Ni_4 cluster (left) and a tetrahedral Ni_3Ti (right), as calculated by the SCF-$X\alpha$-SW method. The SCF-$X\alpha$ 1s orbital energy for atomic hydrogen is also shown.

Using the above results, coupled with the electronic structure of Ni_3Ti shown in Fig. 1 and Table 1, we make the following observations with regards to the interaction of atomic hydrogen with Ni_3Ti cluster.

1) One of the outstanding effects of alloying Ni with Ti is to raise the whole energy spectrum upward with respect to the H 1s orbital. Yet the shift is not uniform; it is more for d-like

Table 1. Energies, occupancies and fractional partial-wave character for the molecular orbitals of a tetrahedral Ni_3Ti cluster, as determined by the spin-restricted SCF-Xa-SW method. Orbital energies in Ry. Occupancies and charges in electrons.

Orbital (occupancy)	Energy	Fractional principal partial wave character					
		Ni			Ti		
		S	P	d	S	P	d
$6a_1$ (0)	-0.185	0.01	0.10	0.09	0.06	0.07	0.27
8e (0)	-0.207	0.03	0.06	0.06	0.01	0.06	0.44
7e (0)	-0.265	0.01	0.03	0.07	—	—	0.12
$5a_1$ (1)	-0.269	0.01	0.03	0.09	0.05	0.01	0.56
6e (1)	-0.270	0.03	0.03	0.16	0.01	0.02	0.30
$2a_2$ (2)	-0.314	—	—	0.32	—	—	0.01
5e (4)	-0.339	—	—	0.32	—	—	0.01
$1a_2$ (2)	-0.340	—	—	0.33	—	—	0.01
4e (4)	-0.342	0.01	—	0.31	—	0.01	0.01
3e (4)	-0.372	0.01	—	0.26	—	—	0.16
$4a_1$ (2)	-0.380	—	—	0.31	0.01	—	0.02
2e (4).	-0.385	—	—	0.31	—	—	0.07
$3a_1$ (2)	-0.404	—	—	0.30	0.02	—	0.02
1e (2)	-0.410	0.02	—	0.26	0.01	—	0.12
$2a_1$ (2)	-0.417	0.02	—	0.26	0.01	—	0.11
$1a_1$ (2)	-0.502	0.15	0.02	0.11	0.06	0.01	0.10

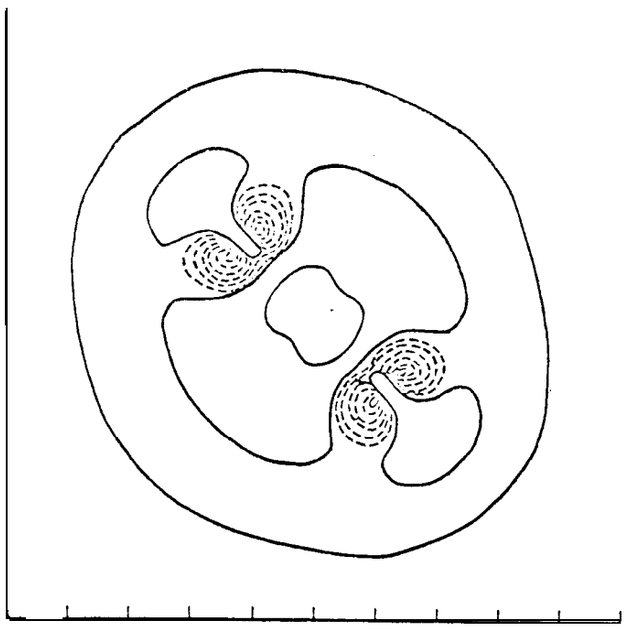

Fig. 2. Contour map for the lowest occupied orbital $1a_1$, in the tetrahedral Ni_4 cluster,. plotted in a plane containing two Ni atoms.

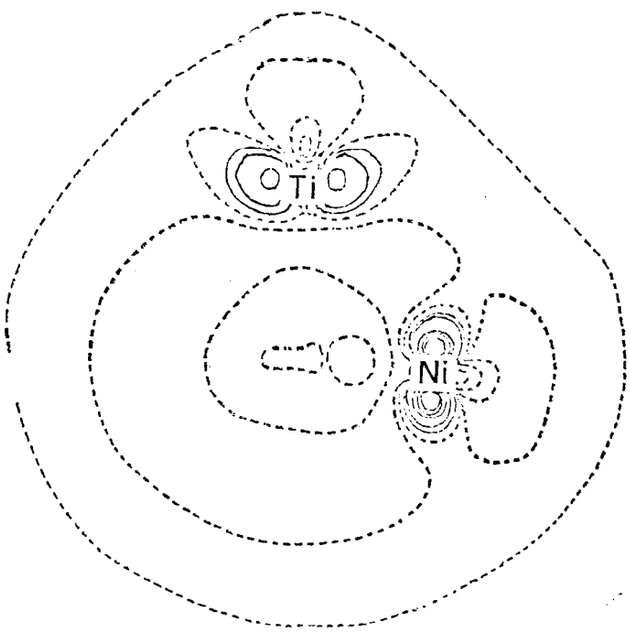

Fig. 3. Contour map for the lowest occupied orbital $1a_1$ in tetrahedral Ni_3Ti cluster, plotted in the plane bisecting the tetrahedron and passing through the Ti atom and one of the Ni atoms.

Table 2. Partial-wave decomposition of the metal-atom contributions to the la, molecular-orbital charge distributions of tetrahedral clusters.

Cluster	Orbital Energy (ε in Rydberg)	Fractional partial wave character		
		S	P	d
Ni_4	−0.528	0.49	0.06	0.45
Ni_3Ti	-0.502	0.52 (0.47Ni, 0.05Ti)	0.06	0.42 (0.38Ni, 0.03Ti)

orbitals (the center of gravity of d-band shifts about 0.037 Ry) and less for the symmetry-conserving la, orbital (0.026 Ry). This uneven shift pushes the d-band further away from the H1s level and the $1a_1$ orbital becomes more of a determining factor in the interaction of Ni_3Ti cluster with atomic hydrogen than it is in Ni,.

2) According to Hume-Rothery[6], the solubility of an impurity in metal generally decreases with increasing electronegativity difference between solute and solvent, if other factors like atomic size remain constant. Since the energy separation between the $1a_1$ orbital and the H 1s orbital increases upon alloying, thus the difference in electronegativity also increases[5], the solubility of hydrogen will decrease in Ni_3Ti compared to that in Ni_4, if electronegativity is the sole factor.

3) In going from Ni_4 to Ni_4Ti, the la, orbital becomes more delocalized as shown in Figs. 2 & 3. This means that the la, orbital in Ni_3Ti overlaps and interacts more with H Is orbital than it does in the case of Ni_4.

4) The partial-wave decomposition for $1a_1$ orbital listed in Table 2 shows that the metallic 4s-like component of $1a_1$ orbital in Ni_3Ti becomes more dominant in bonding of hydrogen to the cluster than does its counterpart in Ni,. This result is consistent with the fact that $1a_1$ orbital in Ni_3Ti is more diffused than la, orbital in Ni_4.

Besides the catalytic activity of Ni_3Ti shown in its interaction with atomic hydrogen, the electronic structure of Ni_3Ti also presents itself with other interesting catalytic properties. In Table 1 the fractional principal partial-wave character for each Ni and Ti atom is listed. It is clearly seen from this Table and Fig. 1 that like transition metal clusters, the electronic structure of Ni_3Ti is also characterized by an approximately half-filled d-band but with some distinctive features. The occupied part of d-orbital manifold is primarily localized spatially on Ni site and the unoccupied part primarily located on Ti sites. This suggests that an electron-donating absorbate would tend to bond to a Ti site, whereas an electron-accepting absorbate would tend to bond to a Ni site. A good example would be Co chemisorption on Ni_3Ti, which is worthy of further experimental and theoretical investigation.

An approximately half-filled d-band is a standard electronic configuration for pure transition metals such as iron, which is an excellent catalyst for some reactions, e. g., ammonia and Fischer-Tropsch Synthesis. However, for Ni_3Ti we have a situation in which the existence of an approximately half-filled d-band is closely associated with the spatial localization of the occupied and unoccupied portions of this band on different surface sites. This local separation of electron doner and acceptor orbitals on a transition metal surface offers the possibility for novel surface chemical properies, which may have exciting catalytic implications.

(5) It was pointed out by K.H. Johnson (Int. J. Quantum Chem. 11S, 39 (1977)) that SCF-$X\alpha$ atomic and molecular orbital energy eigenvalues can be rigorously identified with differential orbital electronegativities. Thus the relative positions of the SCF-$X\alpha$ orbital energies for the Ni_4 and Ni_3Ti clusters with respect to the SCF-$X\alpha$ IS orbital energy for atomic hydrogen, as shown in Fig. 1, are a measure of the differences in orbital electronegativity and chemical potential between these metal aggregates and atomic hydrogen.

(6) W. Hume-Rothery, The Structure of Metals and Alloys (Institute of Metals, London, 1936).