Explanation of the Invar Anomalies from Molecular-Orbital Cluster Calculations

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The electronic structures of pure and mixed Fe-Ni metal clusters, as computed with the self-consistent-field $X\alpha$ scattered-wave method, are used as models for the bonding situation in fcc Fe-Ni alloys. The calculations indicate that several anomalous properties of the Invar alloy $Fe_{64}Ni_{36}$ are a consequence of the presence, at the Fermi level, of strongly antibonding majority-spin orbitals and nonbonding minority-spin orbitals in this concentration range.

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Some magnetic materials have an unusually small thermal expansion coefficient, most notoriously so the fcc Fe-Ni (36% Ni) alloy ("Invar").[1] This anomaly is not isolated but is rather one particular aspect of a more general deviation from "normal" behavior.[2] In this Letter we will discuss only the case of the Fe-Ni alloys which exhibit, among others, the following peculiarities: (1) The thermal expansion coefficient is extremely small in the range of 30–40% Ni.[3] (2) The lattice constant is a maximum for the 40% Ni alloy.[4] (3) There is an abrupt drop in the compressibility as the Ni concentration increases over about 40%.[5] (4) The average magnetic moment as a function of composition deviates from the Slater-Pauling curve, possessing a maximum near 40% Ni.[6,7] (5) The magnetic moments decrease more rapidly with temperature[6,7] and pressure[8] in the Invar concentration range. (6) The electronic contribution to the specific heat is very large for the Invar alloys.[9,10] (7) The forced magnetostriction shows a maximum at 30% Ni.[11] (8) Replacement of Ni atoms by Mn atoms in the Invar alloy leads to a contraction of the alloy, a decrease in the average magnetic moment, and an increase in the thermal expansion coefficient.[12]

Some of these anomalous properties have been interpreted in terms of phenomenological theories with use of either local or itinerant-electron models. The local models[13,14] postulate two kinds of states, a ferromagnetic state associated with a large volume, and an antiferromagnetic one assoicated with a small volume. The Invar effect is then explained by assuming that in the Invar concentration range temperature favors the second state and thereby the normal anharmonic vibrational lattice expansion is counterbalanced. The itinerant theory interprets the Invar effect as a consequence of weak itinerant-electron ferromagnetism.[15,16] While these theories have succeeded to a certain extent in rationalizing the Invar behavior, they do not derive from first principles and each suffers, in our opinion, from serious drawbacks which will be discussed in detail elsewhere.[17] The local-moment theories introduce vaguely defined regions of antiferromagnetic order in the alloys. Though there is a tendency for iron-rich alloys to become antiferromagnetic, at 36% Ni the alloy is, in fact, ferromagnetic.[2,18] The justification for the itinerant theory is the dependence of the magnetization on applied magnetic field and temperature. In other respects, however, the Invar alloy does not seem to be a typical weak ferromagnet.[19]

In this Letter we show the following:

(1) The anomalies of the Fe-Ni alloys can be understood in terms of quantum chemical concepts.

(2) These anomalies result from the ferromagnetic electronic structure of the Fe-Ni alloys; antiferromagnetism is neither essential nor probable.

(3) The physical basis of the phenomenological theories is a rather peculiar situation at the Invar Fermi level where strongly antibonding majority-spin orbitals and nonbonding minority-spin orbitals lie closely together. We show that this situation exists only over a narrow range of Ni concentration.

(4) The Invar alloy can be considered a weak ferromagnet in the sense that both majority- and minority-spin d bands are partially unoccupied.

Our approach was guided by the (well-founded) conviction that the chemical as well as magnetic properties of the transition metals are local not on an atomic scale (as in the Heisenberg and Hubbard models) but rather on the scale of metal clusters.[20-22] The study of such clusters with the self-consistent-field $X\alpha$ scattered-wave (SCF $X\alpha$ SW) method[23,24] allows us to bridge, to a certain extent, the traditional views of local and itinerant theories.

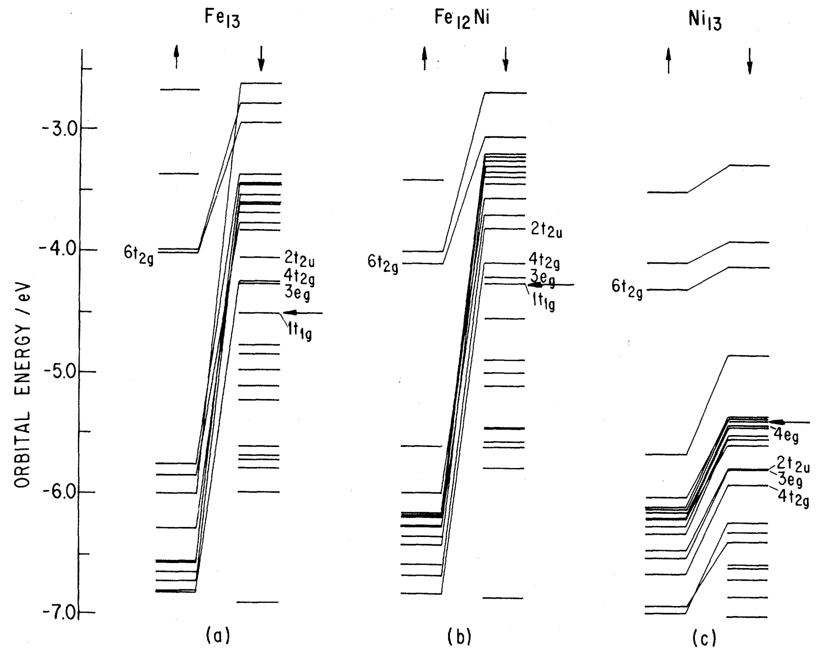

FIG. 1. Orbital eigenvalues from spin-polarized SCF-$X\alpha$-SW calculations for (a) Fe_{13}, (b) $Fe_{12}Ni$, and (c) Ni_{13}.

The one-electron states of several thirteen and nineteen-atom clusters with the fcc structure have been calculated for various compositions and lattice parameters. Full details will be presented elsewhere.[17] In Fig. 1, we show the orbital eigenvalues for Fe_{13} ($a_0 = 3.54$ Å), $Fe_{12}Ni$ ($a_0 = 3.54$ Å), and Ni_{13} ($a_0 = 3.52$ Å). The crucial aspect of these energy-level diagrams is the energy position of the majority-spin $6t_{2g}{\uparrow}$ level which is strongly antibonding (Fig. 2). (The bonding characteristics of the orbitals were inferred from their nodal structure as well as from their energy change with lattice expansion.) In Fe_{13} the exchange splitting is large (2.5 eV) and the $6t_{2g}{\uparrow}$ level is juxtaposed with minority-spin d levels of essentially nonbonding character; in Ni_{13}, where the exchange splitting is small (0.7 eV), this level is well above the d bands.

Because of the similarity of the Fe_{13} and $Fe_{12}Ni$ energy diagrams, and recognizing the uncertainties of both the computational approach and the cluster model in explaining bulk properties of alloys, we will base the discussion on the somewhat arbitrary assumption that the energy diagram of Ni_{13} is typical for nickel-rich alloys and that the bonding characteristics of the iron-rich alloys are well represented by a single "rigid level" scheme which differs from the diagrams in Fig. 1 only in that $6t_{2g}{\uparrow}$ level is placed between the $4t_{2g}{\downarrow}$ and $2t_{2u}{\downarrow}$ levels [an order that is actually found in a pure Fe_{13} cluster with a larger lattice constant, $a_0 = 3.68$ Å (Ref. 17)]. A slightly different ordering of the levels would not change the qualitative aspects of our arguments. Starting with pure Fe (one electron in the $1t_{1g}{\downarrow}$ level) the range of Ni concentrations is simulated by filling

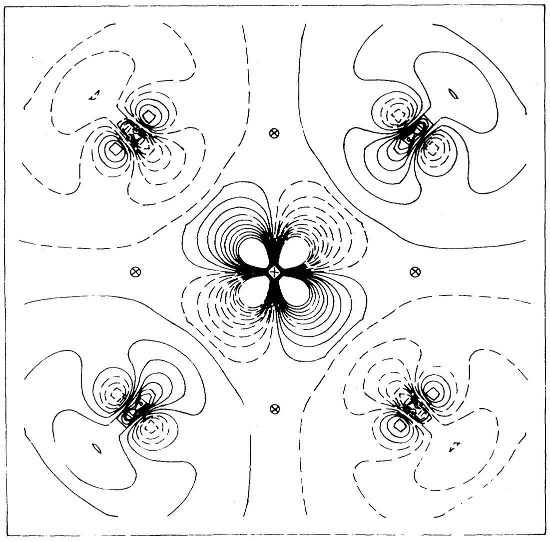

FIG. 2. Contour map of the $6t_{2g}^{\uparrow}$ wave function of Fe_{13}. Negative values are indicated by dashed contours.

electrons into the empty orbitals. For example, the replacement of one Fe atom by a Ni atom in the cluster, which means two more electrons, corresponds to an increase of 7.7% in the Ni concentration. Filling the $1t_{1g}\downarrow$, $3e_g\downarrow$, and $4t_{2g}\downarrow$ levels yields the 27% alloy. Above 27% Ni, additional electrons start to occupy the $6t_{2g}\uparrow$ level. Because of the antibonding nature of this orbital, the lattice will expand, and because it is a majority-spin orbital the average magnetic moment will increase. At 38.5% Ni the level is fully occupied and additional electrons have to occupy the $2t_{2u}\downarrow$ level and higher nonbonding minority-spin orbitals. Hence the magnetic moment will decrease; but so will the exchange splitting. This again destabilizes the $6t_{2g}\uparrow$ level, which consequently will become empty over a narrow range of Ni concentration. Further increase of the Ni concentration results in a contraction of the lattice because the antibonding state is now empty and also because of the smaller atomic volume of Ni. It follows that both the lattice constant and the magnetic moment should have a maximum around 40% Ni. The density of states at the Invar Fermi level is high (Fig. 1), consistent with the large electronic contribution to the specific heat.

In our model, the Invar effect is a consequence of thermal excitations of electrons from the antibonding majority-spin level into the close-lying nonbonding minority-spin orbitals. Emptying the antibonding orbital results in a contraction of the bonds which counteracts the vibrational lattice expansion. Another immediate consequence is that the magnetic moment in the concentration range for which the $6t_{2g}\uparrow$ level is occupied should decrease with temperature faster than for higher concentrations. Also, because of the closeness of majority-spin and minority-spin orbitals the Invar alloy should behave like a weak ferromagnet. For higher concentrations of Ni the majority-spin level is empty once again and the alloys are strong ferromagnets. For concentrations lower than about 30% the magnetic moment may actually increase with temperature because of the possibility of excitations into the $6t_{2g}\uparrow$ level. This would also increase the lattice constant with temperature which might explain the asymmetry of the dependence of the thermal expansion coefficient on the Ni concentration.[3]

Pressure should destabilize an antibonding level; consequently, the compressibility of alloys in the Invar region should be enhanced since electrons will be transferred from antibonding to nonbonding orbitals. Also the average magnetic moment should decrease faster with pressure than in alloys above 40% Ni.

Application of a magnetic field should stabilize the majority-spin orbital and allow or increase its occupation; the resulting lattice expansion (forced magnetostriction) should be strongest for Ni concentrations around 30% Ni where the level is empty or almost so.

Another way of emptying the $6t_{2g}\uparrow$ level is to replace Ni atoms by Mn atoms in the $Fe_{64}Ni_{36}$ alloy. Although Mn atoms are usually considered to be larger than Ni atoms, our calculations would predict a counteracting contraction of the lattice and a simultaneous decrease in the average magnetic moment. Furthermore, the thermal expansion coefficient should increase as Mn is added, becoming normal in the alloy $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ for a value of x around 0.2 because the $6t_{2g}\uparrow$ level will then be empty. This follows simply from the fact that the $6t_{2g}\uparrow$ level holds three electrons and hence if one Ni atom is replaced by a Mn atom the level will be emptied. Since 36% Ni corresponds roughly to five Ni atoms in a thirteen-atom cluster the resulting ratio of Mn:Ni is 1:4 ($x = 0.2$). A similar behavior would be expected if Ni is replaced by Cr, the critical value of x being about 0.15. Indeed, the magnetization of $Fe_{65}(Ni_{1-x}Cr_x)_{35}$ decreases between $x = 0$ and $x = 0.15$.[25] Measurement of further properties in the Fe-Ni-Cr system would be of clear interest.

Hence, all of the Invar anomalies mentioned above can be qualitatively accounted for in a simple manner on the basis of the local electronic and magnetic structure of a series of cluster models. Extensions of these ideas to other alloys and other properties are currently being examined.

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Observation of Charge-Transfer States for Pyridine Chemisorbed on Ag(111)

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The excited states of chemisorbed pyridine on Ag(111) have been determined with use of electron-energy-loss spectroscopy. In addition to weakly perturbed molecular states we observe new excitations above ~1.4 eV, which we identify as metal-molecule charge-transfer excitations. These new electronic states provide an explanation for several features observed in surface-enhanced Raman scattering.

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Here we report the first measurements of the excited electronic states of a surface-enhanced Raman system, pyridine chemisorbed on Ag(111), using electron-energy-loss spectroscopy. We observe weakly perturbed states for chemisorbed pyridine as well as a new ~1-eV broad onset excitation feature starting above ~1.4 eV. The latter represents a new excitation of the metal-molecule system which we assign to charge-transfer excitations between the molecule and metal surface. Information regarding the changes in molecular excitations[1,2] as well as the possible occurrence of new electronic states for chemisorbed molecules[3,4] has been lacking and is needed to clarify and understand the origins of the chemically derived, localized components of surface-enhanced Raman scattering.[5,6] Our results demonstrate the occurrence of new electronic states which (a) will enhance the effective polarizability of chemisorbed pyridine, (b) can permit resonance Raman scattering, and (c) explain several features observed in surface-enhanced Raman scattering. We note that low-lying excitations (1.5–2.0 eV) for pyridine on Ag electrodes[7,8] and small particles in solution[9] have been observed by use of optical methods and have been proposed to arise from several different physical origins.[7-9]

These measurements were performed in a UHV system (base pressure $<1\times10^{-10}$ Torr) equipped with a hemispherical-deflector–based electron monochromator and energy analyzer described elsewhere.[10] This spectrometer has a fixed scattering angle of 90° and collects a well-defined (~0.2-mm-diam) collimated electron beam ($<1°$) reflected from the sample. This sample which is cooled to 140 K can be rotated to observe both specular ($\theta_{\rm in}=\theta_{\rm out}$) and off-specular ($\theta_{\rm in}\neq\theta_{\rm out}$) scattering events in the plane of incidence. Beam energies up to 20 eV were used and our resolution was degraded to ~20 meV (full width at half maximum of the specular beam) in order to more clearly observe the generally broad, low-intensity electronic excitations. Vibrational loss spectroscopy performed with this analyzer as well as