

Electronic Structure and Magnetism of CuNi Coherent Modulated Structures

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The electronic and magnetic properties of a coherent modulated structure consisting of three atomic layers each of Cu and Ni perpendicular to $[111]$ were determined from *ab initio* self-consistent spin-polarized energy-band calculations. We predict a substantial reduction in spin magnetization and contact hyperfine fields H_n at the Ni layers (in contrast with enhancements reported earlier from ferromagnetic resonance measurements), charge ($0.1e^-$) and spin ($\sim 0.01\mu_B$) transfer to the Cu sites, and large H_n at the Cu nuclei.

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Considerable interest has been aroused by the observation of greatly enhanced elastic properties of short-wavelength composition-modulated bimetallic films¹ and especially by the significantly larger magnetization density of a short-wavelength (30 Å) CuNi thin composition-modulated film² compared to that of pure Ni as deduced from ferromagnetic resonance experiments. White and Herring³ have proposed that the anomalously large magnetization value is indicative of a complex magnetization distribution, including negative regions, which can substantially increase ferromagnetic resonance frequencies.

In this Letter, we present the first theoretical determination of the electronic structure and magnetic properties of a realistic layered coherent modulated structure (CMS). *Ab initio* self-consistent, semirelativistic, spin-polarized linear muffin-tin orbital (LMTO) energy-band calculations have been carried out on a 50-50-composition CMS consisting of three atomic layers each of Cu and Ni modulated along the $[111]$ direction.² We find no evidence for a complex magnetization distribution. Instead, the spin magnetization of the Ni layers is reduced relative to that of pure Ni: The central Ni layer moment is $0.50\mu_B$ whereas that of the interface Ni layers is $0.37\mu_B$. The large reduction of the "interface" Ni layer moments is consistent with the magnetically dead layers reported earlier for Ni layers deposited on a Cu substrate.⁴ The calculated core-polarization hyperfine fields, H_n , at the Ni sites also show a reduction proportional to that found for the spin magnetization. The small Cu magnetic moments ($\sim 0.01\mu_B$) result in large H_n values which

are substantially larger than any Knight shifts observed for Cu.

Our CMS, shown in Fig. 1, has six atoms per unit cell and four inequivalent layers denoted as "bulk"-like for the central Cu and Ni and "interface" for the remaining Cu and Ni. Since depositions of a metal *A* on a metal *B* result in a lattice constant for the initial layer which is between that of *A* and *B*, we form our CuNi structure with

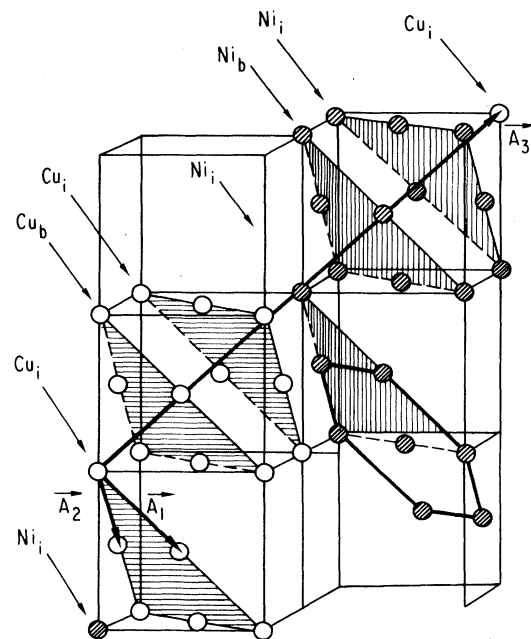


FIG. 1. CuNi CMS modulated along $[111]$ (without local strain). \vec{A}_1 , \vec{A}_2 , and \vec{A}_3 define the six-atom unit cell; *i* and *b* denote "interface" and "bulk."

a lattice constant in the (x, y) plane perpendicular to the modulation as the average of the mismatch (1.25%) of the pure fcc Ni and Cu values. We have ignored the presumed expansion (contraction) of Cu (Ni) in the z direction because of the lack of structural data. The Wigner-Seitz radii, R_{WS} , follow the local lattice expansion (contraction) and are 2.664 and 2.598 a.u. for Cu and Ni, respectively. Since these values are very close to the R_{WS} values for the pure fcc cases, a direct study of charge transfer can be made.

The energy bands of the CuNi CMS and the pure fcc (and tetragonal) Ni and Cu metals were determined self-consistently using the LMTO method.⁵ To allow comparisons, both paramagnetic and ferromagnetic calculations were carried out using, respectively, local-density⁶ and local-spin-density⁷ exchange-correlation potentials. All atoms in the unit cell and all electrons were included in each iteration, with the valence electrons treated semirelativistically⁸ and the core states treated fully relativistically with use of 18 k points in the irreducible part of the hexagonal Brillouin zone. The final calculations used 165 independent k points.

The density-of-states (DOS) diagrams for the (paramagnetic) layer projected d bands normalized to the number of states per atom, shown in Fig. 2 for the CuNi CMS, are obtained from a k -point-weighted histogram. The Cu and Ni bulk (central) atoms, with roughly three separate peaks, have a DOS quite similar to that of the pure fcc metals, while the interface atoms show a lack of structure in their DOS functions. The interface states apparently broaden, and thus lower, the Ni DOS peak at E_F in CuNi relative to that for both pure and bulk Ni. The shape of the interface DOS function still resembles that of bulk DOS which shows that the interface hybridization is not large enough to wipe out the distinct Cu- and Ni-like features of the interface atoms. There is a small charge transfer of about 0.1 electron per atom from the Ni to Cu atoms. Comparison with our results calculated for the pure fcc metals shows that the d -band occupation is unchanged and hence it is the s and p electrons which contribute to the charge transfer.

The overall trends in the DOS, charge transfer, and other results determined in the paramagnetic band calculation are found to remain in the ferromagnetic (spin-split) band results. The most striking result from the spin-polarized data is the partial quenching of the magnetization at the Ni interface sites (to $0.37 \mu_B$) from that calcu-

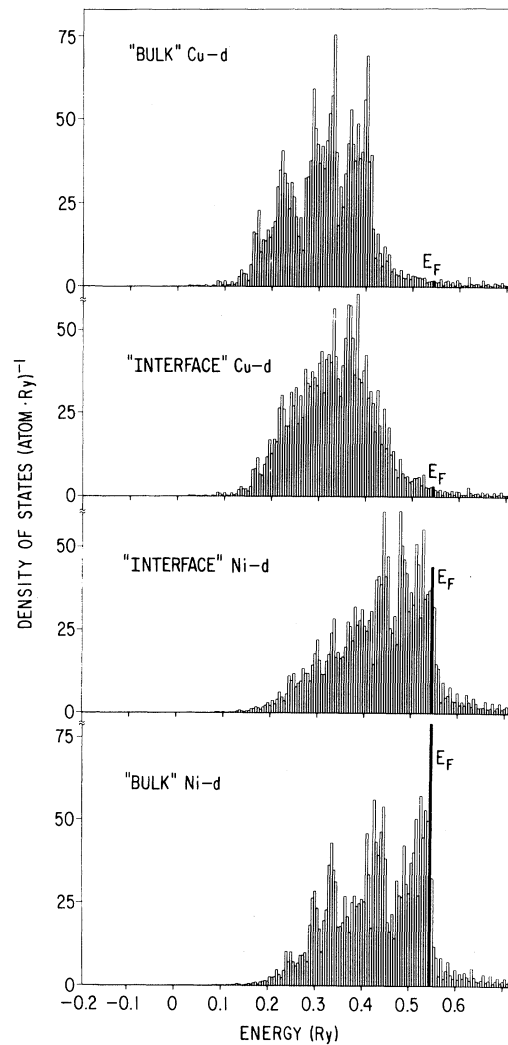


FIG. 2. DOS for the paramagnetic d bands, in units $(\text{Ry} \cdot \text{atom})^{-1}$.

lated for pure Ni ($0.54 \mu_B$) (see Table I). The magnetization at the Ni bulk sites is also reduced but to a lesser extent ($0.50 \mu_B$).

To study the origin of the reduced magnetization on the central layers, we carried out separate calculations for bulk Ni subjected to the tetragonal lattice strain expected⁹ in the CuNi CMS (including the contraction in the $[111]$ direction). Since these local-spin-density calculations give a spin magnetization ($0.46 \mu_B$) which is close to the value found for the bulk Ni layers in CuNi, the reduction from the fcc Ni magnetic moment is seen to be due in part to the strained environment. The reduced magnetization on the Ni interface layers is interpreted to result from hybridization effects at the CuNi interface rather than

TABLE I. Spin magnetization per atom and l projection.

	s	p	d	total
Cu _b	0.002	0.005	0.003	0.009
Cu _i	-0.000	-0.004	0.008	0.005
Ni _i	0.002	-0.001	0.373	0.374
Ni _b	0.001	-0.002	0.505	0.504
Ni(fcc)	-0.003	-0.016	0.554	0.536

to arise from charge transfer or local strain effects. The interface states, which have washed out the peak at E_F , make a Stoner splitting of the local paramagnetic band structure energetically less favorable. Our results are consistent with previous studies of the formation of magnetically dead layers when Ni is deposited onto a nonmagnetic substrate⁴ like Cu. In these experiments, no magnetization appears until 2.5 or more Ni layers are deposited.

We have calculated the contact hyperfine fields H_n at the Ni sites arising from the exchange polarization of the core and conduction electrons.^{10,11} As seen from Table II, the core contributions to H_n on the Ni bulk and interface sites are exactly proportional to the Ni $3d$ spin magnetic moments listed in Table I. [The proportionality to the pure fcc Ni is not so precise because of an additional core-polarization contribution (~ 4 kG) coming from the small $4p$ moment ($-0.02 \mu_B$).] Since H_n is sensitive to the radial shape of the $3d$ spin density,¹⁰ this proportionality indicates that the $3d$ spin densities at the two Ni sites in CuNi and in fcc Ni closely resemble each other. Further, since their core-polarization fields per unpaired spin are close to the free-ion results,¹¹ the $3d$ spin densities are also apparently spatially localized. Both these expectations are confirmed in our calculations which show the $3d$ spin densities to be essentially indistinguishable when plotted (except for a small negative-density region near the R_{WS} for fcc Ni). Hence neutron magnetic scattering experiments can use the same magnetic form factor for both Ni sites to deduce their magnetic moments. The valence contribution to H_n is sensitive to the hybridization effects with the Cu and changes sign compared to the fcc Ni. Thus the reduction of the total H_n is stronger than the reduction of the magnetic moments at the Ni sites.

Our work also gives the first evidence for the formation of small magnetic moments ($\sim 0.01 \mu_B$)

TABLE II. Contact hyperfine fields in kilogauss.

	Core	Valence	Total
Cu _b	0	+11	+11
Cu _i	-1	-6	-7
Ni _i	-55	+7	-48
Ni _b	-75	+11	-64
Ni(fcc)	-78	-12	-90

at the Cu sites. As seen from Table II, although small, the moments on the Cu sites result in substantial H_n due almost entirely to the conduction-electron spin density at the central sites (11 kG) and interface sites (-7 kG). These H_n values are much larger than any Knight shifts and should, in principle, be observable by NMR. Another possibility is an AuNi CMS since the transferred H_n on the Au sites should be observable as a broadening of the Au¹⁹¹ Mössbauer spectrum. Coherent modulated systems such as FeCu are also likely candidates for observing, using NMR, any large transferred hyperfine fields on the finite number of different Cu layer sites.

Finally, we do not know the reason for the disagreement between our substantially *reduced* spin magnetic moment values and the substantially enhanced magnetization deduced from the ferromagnetic resonance experiments.² We see no evidence of a complex magnetization distribution which White and Herring³ have invoked to explain the much higher ferromagnetic resonance frequencies. However, just completed direct magnetization¹² and neutron-diffraction¹³ measurements have confirmed our predictions of a reduction of the moments per Ni atom over that of pure Ni, and hence the validity of the local-spin-density approach for describing the electronic structure and magnetic properties of modulated metallic films.

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Surface Core-Level Binding-Energy Shifts for GaAs(110) and GaSb(110)

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Surface $3d$ and $4d$ core-level binding-energy shifts have been resolved in photoemission from GaAs(110) and GaSb(110), which yield new information on semiconductor surface reconstruction. The shifts (~ 0.3 eV) are toward higher (lower) binding energies for the surface cations (anions), in agreement with a simple model involving the known surface relaxation of GaAs(110) with a geometry-dependent initial-state charge transfer. Surface core-excitation binding energies, core-level widths, escape depths, etc., are reevaluated.

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We have observed shifts in the $3d$ and $4d$ core-level photoemission binding energies of surface-layer atoms relative to bulk atoms for the (110) cleavage surfaces of GaAs and GaSb. Recently, such shifts have been reported for several $5d$ metals.¹⁻³ These surface binding-energy shifts, which measure the change in the electrostatic potential at the core, yield new information on charge redistribution in the surface layer which accompanies the large reconstruction and/or relaxation that invariably occurs for semiconductors.⁴ GaAs(110) is the prototype surface since its atomic structure is the best understood of any semiconductor; there is general agreement that surface As atoms move outwards and surface Ga atoms move inwards, with a $\sim 25^\circ$ bond-angle rotation^{5,6} and a charge transfer from Ga to As surface atoms.⁷ For GaAs(110), we find that the surface Ga $3d$ level is shifted to larger binding energy by $\Delta E_B = +0.28$ eV, while the As $3d$ level is shifted to smaller binding energy by $\Delta E_B = -0.37$ eV relative to their bulk counterparts. Compar-

able binding-energy shifts are observed for GaSb(110): $\Delta E_B(\text{Ga } 3d) = +0.30$ eV and $\Delta E_B(\text{Sb } 4d) = -0.36$ eV.

To our knowledge, the only calculations of such geometry-dependent binding-energy shifts for semiconductors are *ab initio* valence-band calculations using small clusters which have been used to study the reconstruction and/or relaxation and oxidation of GaAs(110).⁴ Barton, Goddard, and McGill⁴ have reported core-level shifts of $\Delta E_B(\text{Ga } 3d) = -0.19$ eV and $\Delta E_B(\text{As } 3d) = +0.24$ eV for relaxed surface atoms (25° bond-angle rotation) relative to unrelaxed surface atoms. However, these shifts (of opposite sign) cannot be directly compared to our experimental shifts, which are measured relative to bulk atoms. Semiconductor surface core-level shifts relative to bulk atoms have not been calculated using *ab initio* self-consistent methods for lack of experimental data. However, tight-binding calculations have estimated that the surface relaxation is accompanied by a charge transfer from Ga to As surface