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Spin-Dependent Density of States in Ferromagnetic Ni-Fe Alloys

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Experimental spectra of spin-polarized photoemission from well-defined $Ni_{1-x}Fe_x$ (100) surfaces for $x = 0.2$ and 0.6 are presented. They reflect the difference between occupied up- and down-spin densities of states of the bulk near the Fermi energy. It is shown that the majority bands are not full for $x = 0.6$, in contrast to $x = 0.2$ and pure Ni, and that the majority density of states dominates at the Fermi energy for $x = 0.6$. Current theories of ferromagnetic alloys do not fully account for the observed spin polarization.

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The deviation of the magnetization from the Slater-Pauling straight line at a concentration of ~50% Fe in fcc Ni-Fe alloys has been of great interest for many years. It is a crucial test of any theory of itinerant-electron magnetism in ferromagnetic alloys on one hand and it marks the onset of the Invar regime on the other hand. The ferromagnetism of the pure metals Ni and Fe is relatively well understood at present. New theories exist which give at the same time correct magnetic moments, correct Curie temperatures, and a Curie-Weiss behavior.[1] Also spin-polarized photoemission spectra of Ni,[2,3] on the experimental side, can now be fairly well interpreted in the framework of a one-electron theory with underlying bulk[4] or surface-specific[5] ferromagnetic band structures.

On the basis of the recently advanced understanding we decided to apply spin-polarized photoemission to the Ni-based fcc substitutional alloy $Ni_{1-x}Fe_x$ with the aim to gain first experimental information on the spin dependence of the bulk density of states (DOS) in the vicinity of the Fermi level E_F. We present studies on well-defined $Ni_{0.8}Fe_{0.2}$ and $Ni_{0.4}Fe_{0.6}$ single-crystal (100) surfaces covered with ≤ 0.2 monolayers of K. The conclusion is reached that in $Ni_{0.4}Fe_{0.6}$ the majority band is not full, in contrast to $Ni_{0.8}Fe_{0.2}$ and pure Ni, and that this is a property of the bulk. The deviation of the magnetization from the Slater-Pauling straight line must then be discussed by considering the occurrence of majority holes as was first predicted by Hasegawa and Kanamori.[6] The spectra of spin polarization near photothresh-

old reported in this Letter are a base for the further development of the theories of crystalline ferromagnetic alloys. Local-environment effects will have to be treated together with unfilled majority spin bands, which is one step beyond present day calculations of ferromagnetic alloys. Very recently Kaspar and Salahub have presented a calculation of molecular orbitals from first principles of Ni-Fe clusters[7] which yields a basic qualitative understanding of the Invar properties. Their arguments are corroborated by the present observations.

The technique of spin-polarized photoemission and details of the apparatus have been described earlier.[8] Here we are particularly interested in features near or at the photothreshold. This requires a well-defined homogeneous work function Φ of the sample which only can be achieved by using well-defined single-crystal surfaces. The very good quality single-crystal samples were prepared by O. Scherber, University of Munich, Germany. We cleaned the (100)-oriented surfaces *in situ* by short cycles of 400-eV Ar^+ bombardment[9] at room temperature and annealing at 600 °C. The cycles always were terminated with Ar^+ bombardment and subsequent mild annealing to 200 °C. The quality of the surface was checked with Auger electron spectroscopy and low-energy electron diffraction (LEED). O and C contaminations were found to be below ~5 at.% and no surface segregation was detected. Fairly sharp LEED spots in (1×1) structure with intensity maxima corresponding to pure Ni[10] were observed, indicating that both surfaces are good fcc single crystals without reconstruction. The clean surfaces subsequently were covered with a small amount of K in order to vary the work function of the sample.

The measured spectra of spin polarization $P = (j\uparrow - j\downarrow)/(j\uparrow + j\downarrow)$ versus the difference between photon energy and work function, $h\nu - \Phi$, are presented in Fig. 1. The work function Φ of the samples was lowered by ~1.5 eV through adsorption of a small amount of K. The polarization values at the photothreshold $h\nu - \Phi = 0$ are interpreted as the difference between up- and down-spin DOS of the bulk at the Fermi energy. This calls for justification and before proceeding to the discussion of ferromagnetic alloys we want to address two important questions:

(i) Is the observed spin polarization a property of the bulk or is it to some degree characteristic of the surface electronic structure? From the experimental point of view we see that surface

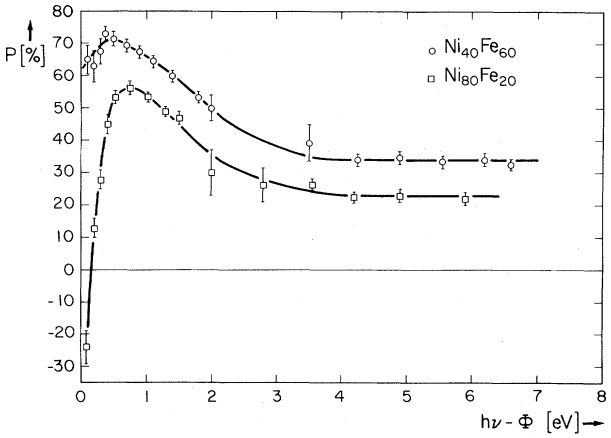

FIG. 1. Spin polarization P vs photon energy minus work function, $h\nu - \Phi$, for $Ni_{40}Fe_{60}$ (100) and $Ni_{80}Fe_{20}$ (100), respectively. The data were taken at 220 K in an external magnetic field of 8.4 kOe. Both sample surfaces were covered with a small amount of K.

states are not detected in spin-polarized photoemission from transition metals. Surface states are very sensitive to contaminations and simply disappear from photoemission spectra upon adsorption of a few percent of O or CO contamination. It takes typically ten hours to collect the data for a polarization spectrum and impurities up to a few tenths of a monolayer are accumulated. The polarization was found to be stable. Thus we conclude that spin-polarized photoemission from transition metals reveals properties of the electronic structure of the bulk and that in the case of pure Ni the Moore-Pendry description[4] is correct. The presence of a K overlayer on the surface does not influence the polarization of photoelectrons beyond the effect of an altered work function. From spin-polarized photoemission using optical pumping it is known that depolarization by an alkali overlayer is negligible.[11]

(ii) Do the reported spectra near photothreshold reflect the difference between up- and down-spin DOS near the Fermi level or is the final-state DOS near the vacuum level likewise important? In pure single-crystal Ni(100) the situation is rather simple since emission at threshold is restricted in phase space to states with k along Γ-X and with the energy of the vacuum level. No direct transitions to such bulk band states exist and the emission takes place via time-reversed LEED states. In single-crystal Ni-Fe alloys the situation is different in that k is broadened because of the disorder in the alloy and thus k conservation is partly lifted in the photoemission

process.[12] Bulk band states at the vacuum level could then play a role. In order to test their influence we covered the surfaces with a variable amount of an alkali metal (K in the present case) which forms a strong electric dipole field and thus reduces the effective work functions of the sample. In Fig. 2 we present spectra for various work functions Φ. We cannot show spectra of the clean samples with $\Phi \simeq 5.3$ eV because of the low intensity of the conventional light sources between 5.4 and 6.8 eV. We observe that the spectra essentially are shifted in excitation energy $h\nu$, specifically, the features at the photothreshold persist upon altering the work function. This proves that final states do not influence the polarization near threshold. We have shown now that the reported spectra near photothreshold can be interpreted in terms of the occupied bulk DOS near the Fermi level.

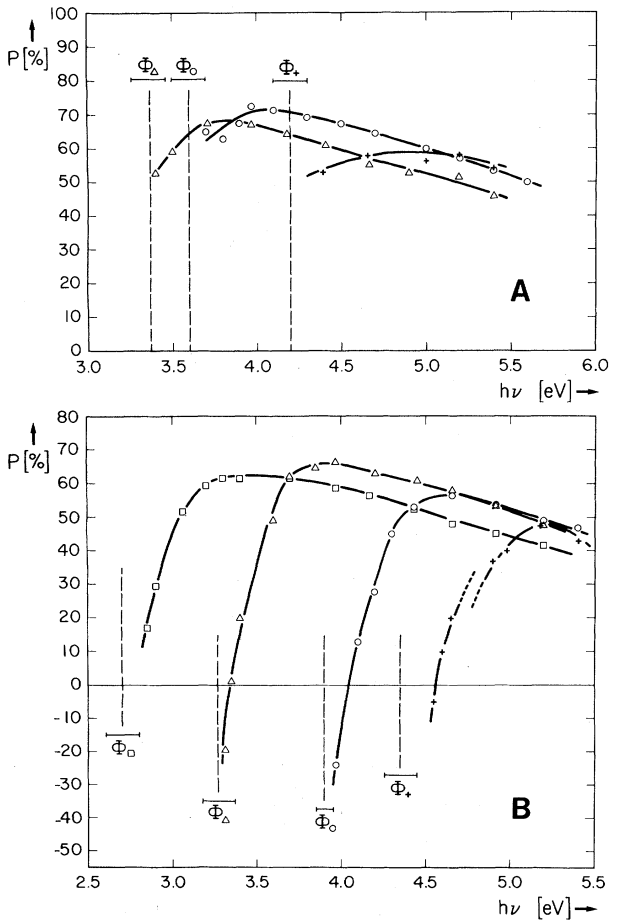

FIG. 2. Spin polarization P vs photon energy $h\nu$ for various work functions Φ. The work function was lowered by covering the surfaces with a variable small amount of K. (a) $Ni_{40}Fe_{60}$ (100), (b) $Ni_{80}Fe_{20}$ (100). The dashed line in (b) reflects a possible increase of Φ caused by K desorption during that particular run.

The fact that majority holes occur in Ni-Fe alloys at the concentration where the magnetization deviates from the Slater-Pauling straight line has long been speculated about.[13] We present here the first direct evidence that this is true. Modern theories of ferromagnetic substitutional alloys can be roughly divided into two groups. The ones[6,14,15] following the pioneering work of Hasegawa and Kanamori[6] use the coherent-potential approximation (CPA) which is a single-site approximation independent of the species of the neighboring atoms. The second group includes the effect of the local atomic environment[16-18] as an extension of the CPA. In the first kind of calculation a set of parameters are used, the most important of which is the exchange splitting Δ of pure Ni. We restrict the present discussion to the effect of the choice of Δ. As has been pointed out by Hennion *et al.*[19] the top of the majority band is found to sink further and further below the Fermi level with increasing Fe content for large Δ values. Only for small Δ's in the neighborhood of 0.35 eV do they find that the Fermi level crosses the majority band at ~50% Fe, in accord with Hasegawa and Kanamori[6] who used $\Delta \simeq 0.35$ eV and with the recent calculation by Inoue, Yamada, and Shimizu[15] who adopted $\Delta \simeq 0.38$ eV. So, the CPA calculations do predict the occurrence of majority holes in Ni-Fe if a very small value of the exchange splitting for the ground state of Ni is used. The spectra we have presented in this Letter contain more information than that. They unambiguously show that at 60% Fe the majority DOS at E_F strongly dominates, a feature which is not reproduced in the latest and most refined CPA calculation.[15]

Local-environment effects are important since the magnetic state of a given atom can be quite sensitive to the composition of its nearest neighbors. Jo has introduced a ternary alloy picture[17] for concentrated ferromagnetic systems. Ni-Fe is described as composed of Ni and two sorts of Fe atoms with parallel and antiparallel magnetic moments. Antiparallel Fe is predicted to occur for higher Fe content and is made responsible for the deviation of the magnetization from the Slater-Pauling straight line. More recently Miwa has presented a study of local-environment effects in Ni-Fe clusters[18] with the result that in an Fe-rich environment antiparallel Fe is stable. In both models the parameters are chosen such that no instability of the parallel Fe moment oc-

curs and consequently the majority DOS at the Fermi level is zero. We find this to be in contrast to the present experimental observation. A recent neutron scattering study, on the other hand, has revealed that the Fe moments at a high Fe concentration indeed are environment dependent.[20] Kaspar and Salahub have tackled the Invar problem with a quantum chemical approach. Recently they presented the results of a spin-polarized self-consistent-field $X\alpha$ scattered-wave calculation of fcc Fe-Ni clusters.[7] They find that in the concentration range of ~40% Ni the presence, at the Fermi level, of strongly antibonding majority-spin orbitals and nonbonding minority-spin orbitals is responsible for various Invar anomalies. At higher Ni concentrations the antibonding majority-spin level is found to be empty. These results are in qualitative agreement with the presently observed sign of spin polarization at the photothreshold of the alloys with 40% and 80% Ni, respectively.

Finally, we wish to give reference to the very recent self-consistent band calculation of Fe_3Ni and FeNi by Williams *et al.* They calculated the volume dependence of the total energy, and they describe Invar as a mixture of the ferromagnetic and paramagnetic states. The calculated state densities of Fe_3Ni exhibit majority holes and they expect a polarization of $P \simeq \frac{1}{3}$ near E_F.[21]

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