

Observation of Highly Enhanced Curie Temperature at Ni-Al Alloy Surfaces

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Detection of a distinct ferromagnetic order at surfaces of Ni-Al solid solutions is reported. By monitoring Lorentz force induced attenuation of the low-energy Auger electron spectrum, the Curie temperature at the annealed Ni-9% Al(110) clean surface has been found 111 K higher than the bulk value, and for Ni-5% Al the enhancement is 58 K. Its origin and the induced attenuation effects are discussed. Ar bombardment or O₂ adsorption shift gradually the surface related transition temperature towards the bulk value.

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Experimental and theoretical studies of magnetic order at the free surfaces of metals have shown that its main characteristics differ remarkably from those of the underlying bulk material [1]. Thin-film and interface magnetism have been also explored extensively in recent years. This includes various magnetic properties, such as the value of the magnetic moment per atom, the Curie temperature and critical exponents, magnetic surface anisotropies, etc. [1-4]. For these goals, specialized experimental techniques have been developed, such as spin-polarized low-energy electron diffraction (SPLEED), electron capture spectroscopy (ECS) [1,4], the surface magneto-optic Kerr-effect technique (SMOKE) [5], etc. The increasing interest in surface, thin-film, and interfacial magnetism stems not only from the unique physical phenomena related to the reduced dimensionality or coordination numbers, but also because of potential technological implications.

In principle, surface enhanced magnetic order is expected in case of significant enhancement of magnetic moments, or of the exchange coupling between spins in the top layer, relative to the bulk spins which remain disordered. Surface Curie temperature enhancements have been observed of 60 and 28 K for the 4f elements Gd [6] and Tb [7], respectively [the issue of a ferromagnetic Cr(100) surface with a highly enhanced T_C is somewhat controversial [2,8]]. For pure nickel, on the other hand, no measurable difference has been noted between the surface and bulk Curie temperatures [9], in spite of 10% to 20% enhancement of the surface magnetic moment estimated in various theoretical studies [3,4].

This Letter reports about the remarkable Curie temperature enhancements of 111 ± 4 and 58 ± 2 K related to the clean surfaces of bulk Ni-9at. % Al and Ni-5at. % Al alloys, respectively. In addition, preliminary results concerning variations in the enhanced temperatures caused by oxygen adsorption and argon bombardment are described. The measurements used a simple method that is based on the deflection of emitted low-energy Auger electrons by Lorentz forces due to stray magnetic fields, which are induced around the sample surface when cooled below T_C in the presence of a magnetizing external field. A

key ingredient devised in this experiment is the application of an effectively magnetizing external field that at the same time is weak enough not to have any direct effect on the emitted electrons. Thus, the method involves a slight variation of a standard Auger electron spectroscopy (AES) experiment (in which magnetic fields are strictly avoided) and, as such, it has the advantage of the concomitant determination of surface composition with a high spatial resolution. Depending on the characteristics of the electron energy analyzer, the deflection can lead to attenuated signals at the detector. The high sensitivity of the attenuation effect to magnetic transitions (shown below) is attributed mainly to the focusing characteristics of the cylindrical mirror analyzer (CMA) used, and to choosing easily deflected, slow electrons as the probe [e.g., the Ni(MVV) Auger emission at 61 eV]. Such electrons have a very shallow mean free path in the solid ($\lambda \sim 0.4$ nm).

Most experiments involved a large area (110) face in a well-annealed polycrystalline Ni-9% Al sample in a form of a small disk (9 mm diameter, 0.5 mm thickness), using a commercial scanning Auger apparatus (PHI 545) with a single-pass CMA and a coaxial electron gun. Room temperature coercivity of ~ 3 Oe and remanence of ~ 70 G were determined for Ni-9% Al using vibrating sample magnetometry. Appropriate external magnetic fields were achieved by passing electrical currents in the range of 1.5 to 3 A through a small filament adjacent to the back side of the sample (Fig. 1, top), which simultaneously control the temperature. The resultant applied fields near the surface center have been estimated in the range of ~ 0.5 to 1 Oe. These small fields are expected to alter locally the domain structure of this magnetically soft material, resulting in induced fields capable of effective electron deflection. The sample surface was sputter cleaned in the UHV chamber (2×10^{-10} Torr base pressure) and annealed for several minutes at ~ 970 K (by electron bombardment), resulting in an equilibrium oscillatory concentration gradient with Al-rich top layer [10]. Figure 1 also shows the low-energy portion of three representative Auger spectra of the annealed Ni-9% Al recorded during cooling. A significant, temperature-dependent signal attenuation can

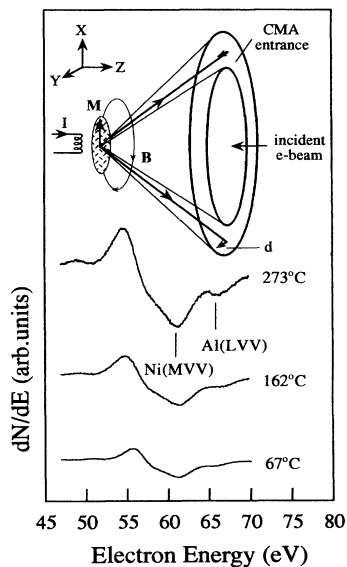


FIG. 1. Top: Schematics of the experimental arrangement for measuring magnetic transitions based on a standard AES apparatus with CMA and *in situ* small electrosolenoid: *I*, current through the solenoid (filament) located ~ 2 mm behind the sample; *M*, resultant net magnetization of sample; *B*, induced flux density; *d*, Lorentz force deflections of emitted electrons entering the CMA (axis along *z*). Bottom: Low-energy Auger spectra of clean Ni-9% Al(110) annealed surface recorded at three temperatures (incident beam energy 3 keV; filament current on).

be noted for both Ni and Al low-energy transitions. As the overall deflection by the sample fields is inversely proportional to the electron velocity, a much greater effect has been observed for Ni(*MVV*) at 61 eV than for the Ni(*LMM*) electrons at ~ 850 eV. Since no contaminants appeared on the alloy surface during the experiment, and since the external current did not affect directly the electron spectrum intensities, the observed attenuations must be intrinsic to the Ni-9% Al partially magnetized sample. Plotting the Ni(*MVV*) signal intensities, or for better accuracy the ratio of the two Ni signals, as a function of temperature reveals the bulk magnetic phase transition at 380 ± 4 K, as well as another sharp attenuation at significantly higher temperature, 491 ± 2 K, identified as a surface-related magnetic transition [Fig. 2(a), discussed below]. This Curie temperature enhancement is not unique to the Ni-9% Al(110) surface, but observed also for other surface orientations in this alloy. A smaller, 58 K enhancement is exhibited by the more dilute Ni-5% Al solid solution [Fig. 2(b)], and the same experiment conducted for pure nickel revealed a single temperature at which an abrupt attenuation of signal intensity occurs [632 ± 2 K, Fig. 2(c)], corresponding to its well-known Curie temperature. The convergence of the observed transitions at the pure Ni value [Fig. 2(c), inset] points out the magnetic nature of both. Moreover, the measured bulk transition temperatures, which decrease more strongly with increasing Al content than the surface related ones, agree well with data measured by a more

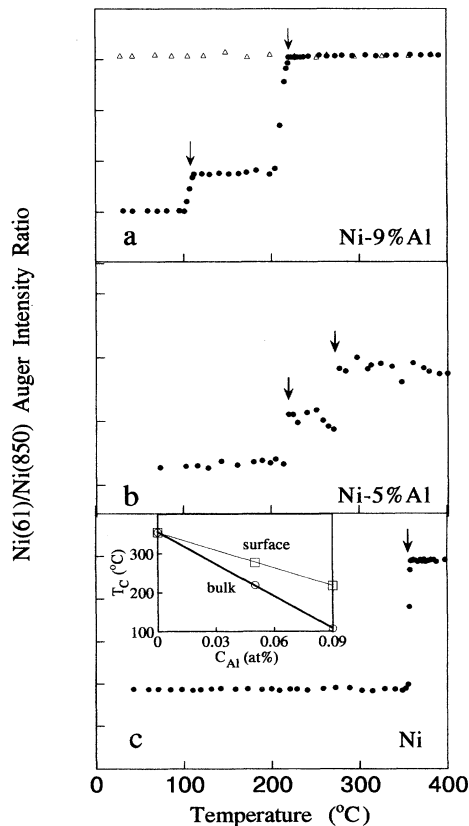


FIG. 2. Auger intensity ratios vs temperature ("attenuation plots") for annealed Ni-9% Al(110) (a), for Ni-5% Al (b), and for pure Ni (c). Inset: Surface-related and bulk transition temperatures vs Al bulk concentration. Intensity ratios measured while keeping the heating (magnetizing) filament off are denoted by Δ in (a). Curie temperatures are marked by arrows exactly above the onset of signal attenuation.

conventional technique [11]. Regarding the shape of the attenuation plots, the invariably attenuated intensity observed upon cooling below T_C (Fig. 2) is attributed mainly to demagnetizing fields acting in the presence of relatively weak external magnetic fields [12,13], resulting in quite an abrupt change of magnetization over only few degrees around T_C . Measurements for the Ni and Ni-Al samples done during heating following cooling under external magnetic field, or reversing its direction, gave similar attenuation plots. It should be noted that the invariance of the signal intensities (i.e., no attenuation) as a function of temperature under zero external field [e.g., Fig. 2(a)] is consistent with the above mentioned origin of the effect, namely, the key role of local stray magnetic fields due to some domain growth and resultant poles, induced by the external magnetic field. Obviously, the induced fields vanish when the surface (or bulk) become paramagnetic upon heating up the sample to the corresponding Curie temperature. In the unmagnetized state of the surface or bulk (cooling to $T < T_C$ without external field) such magnetic fields are either absent (due to closure domains), or have a negligible

effect on the emitted electrons. Separate scanning Auger measurements showed that a $\sim 0.2^\circ$ shift in the Y -axis direction experienced by emitted electron trajectories (see Fig. 1) is sufficient to reduce significantly the signal sensitivity of the CMA used. This accounts for the attenuation effect observed even when the samples were cooled to room temperature under decreasing external fields (Fig. 2), resulting in weak remnant stray fields (around 0.5 Oe) parallel to the surface, as measured for Ni-9% Al *ex situ* using a Hall probe. Because of geometrical factors, this field extends in the region surrounding the surface more than does the filament field, and hence is effective in deflecting electrons.

Several additional factors contribute to the observed high sensitivity of the attenuation effect to surface related magnetic transitions: (i) According to mean-field theoretical predictions, enhanced surface magnetization of a bulk solid is not confined to the first monolayer, but extends somewhat below the surface and decays exponentially with a characteristic length parameter [14,15]. In the present case, simple magnetic intensity calculations taking into account the sample geometry indicate that the highly effective stray fields are due to a thicker magnetic layer, which may be related to the in-depth oscillatory segregation profile of the annealed alloy (alternating Al-rich/Ni-rich layers) [10], or to Ni-rich clusters [16]. Apparently, magnetic order originating with the top surface layers can extend in such a way deeper into the bulk. (ii) Magnetic poles induced by the external field at *local* surface domains are expected to be close to the region of emitted low-energy electrons, and hence corresponding magnetic fields can be of the same order of magnitude as fields from the well-separated poles associated with the (smaller) net magnetization of the macroscopic bulk. (iii) In the experiments described above, bulk magnetic transitions were measured always *after* the respective enhanced T_C . Hence, signal attenuation corresponding to a bulk transition involved an already defocused CMA with electron trajectories undergoing less efficient deflection, related to their orientations with respect to the external field (which was considerably weaker than for the surface related transition). Domain structure measurements for the Ni-Al alloys, as well as simulations of low-energy electron deflection with larger applied fields, will provide a more complete understanding of the attenuation effects.

The identification of the first attenuation [Figs. 2(a)-2(b)] as due to a surface-related magnetic transition is based mainly on the observation that any chemical or structural modification of the surface changes significantly its characteristics, whereas, as expected, the lower-temperature bulk transition is not affected. This is demonstrated for the Ni-9% Al alloy by the effects of oxygen adsorption and of argon bombardment presented in Fig. 3. Even small amounts of adsorbed oxygen ($\sim 2\%$ monolayer, after ~ 0.15 L exposure, $1 \text{ L} = 10^{-6}$ Torr s) induce lowering of the enhanced Curie temperature by about 30 K and the transition becomes less abrupt. This trend continues

with further exposures, until exposure to 100 L O_2 results in a full suppression of the distinct transition [Fig. 3(a)]. Moreover, the overall signal attenuation in this case is similar to the relative attenuation measured for the bulk transition of the clean (or slightly O-covered) alloy, indicating the disappearance of surface related ferromagnetic order. As to ion bombardment effects [Fig. 3(b)], with increasing energy of the impinging argon ions, this transition shifts to lower temperatures concurrently with changes in the shape of the temperature dependence.

Addressing first a possible origin for the clean surface T_C enhancement, we applied the Kirkwood correlation approximation to the semi-infinite, fcc spin- $\frac{1}{2}$ Ising ferromagnet model [17], assuming enhancement of surface magnetic moments in a homogeneous solid solution. Following a procedure outlined in Ref. [14], the system of equilibrium equations was linearized and reduced to a secular equation giving the dependence of T_C^s/T_C^b on the surface to bulk magnetic moment ratio μ_s/μ_b [to simplify the computation, the two topmost (110) planes have been treated as a bulk-truncated, single surface layer with averaged coordination numbers]. For the measured transition temperatures, μ_s turns out to be 55% and 38% larger than μ_b for the 9% and 5% Al solid solutions, respectively (the calculated critical ratio for T_C^s enhancement is 1.17, almost independent of composition). This relative increase of μ_s is well above the μ_s/μ_b ratio calculated for pure nickel [1.13

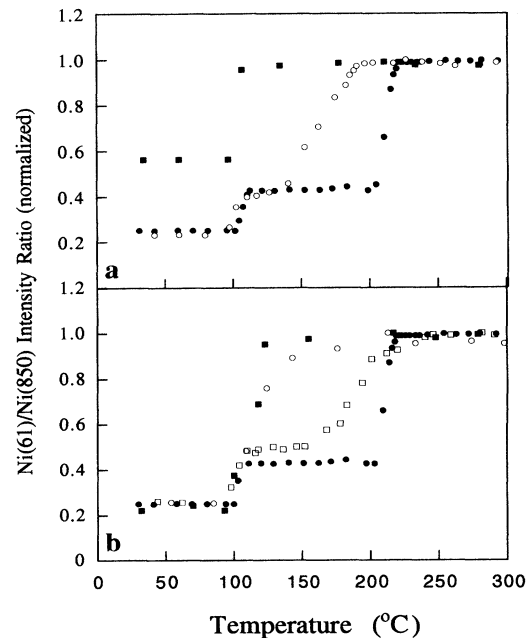


FIG. 3. Normalized attenuation plots (ratios relative to the high temperature value) for modified Ni-9% Al(110) surface: (a) after adsorption of ~ 0.15 L O_2 (\circ) and 100 L O_2 (\blacksquare); (b) after 1 min bombardment with 0.5 keV (\square), 1 keV (\circ), and 2 keV (\blacksquare) argon ions. Prior to each adsorption or bombardment the sample was annealed at 970 K; the corresponding attenuation plot (\bullet) is given for comparison.

for Ni(110) [3]] and evidently, its major part originates from alloying effects. Thus, considering the suppression of Ni magnetization due to increased $sp-d$ hybridization induced by adjacent Al atoms [18], which is also manifested in a monotonous decrease of μ_b with Al bulk concentration [11], the additional μ_s/μ_b significant enhancements in the alloys can be explained by the substantially different Ni-Al coordination at the surface and in the bulk. In particular, the reduced coordination number in a bulk-truncated surface results in diminished hybridization and a weaker decrease of the surface Ni magnetic moment with increasing Al bulk concentration. Consequently, μ_s/μ_b is enhanced compared to the pure Ni value, so that T_C^s can exceed T_C^b . The effect is expected to decrease for smaller Al contents in the solid solution [see experimental evidence in Figs. 2(a)–2(b)], until in pure nickel the two phase transition temperatures coincide [Fig. 2(c) and Ref. [9]]. Furthermore, according to this approach μ_s/μ_b or even T_C^s enhancements may take place in other Ni alloys as well, since hybridization-related fractional change of magnetic moments of Ni atoms depends sensitively on the nonmagnetic environment [1–3,18,19]. However, a greater μ_s relative enhancement can be anticipated when nickel is alloyed with normal metals (e.g., Al), compared to Cu or noble metals, because of a stronger coupling of the Ni d band with the normal metal sp bands, resulting in greater decrease of magnetic moments with alloying element concentration [11,18]. Further changes in the μ_s/μ_b ratio (or in the respective coupling constants) may occur because of possible inward relaxation of the Ni surface atoms, such as the 6% contraction reported for NiAl(110) [20]. However, such effects are probably minor compared to the coordination number effects [17]. Additional calculations of the enhancement effects that take into account alloy inhomogeneities, such as the surface segregation oscillatory gradient and possible Ni clustering, are in progress.

The fine features of the Ni(MVV) and Al(LVV) Auger spectra furnish means to characterize the alloy interactions with adsorbed oxygen. In particular, Al is preferentially oxidized even at very low coverage of oxygen while Ni remains metallic with, perhaps, some chemisorbed oxygen. On the other hand, after 100 L O₂ exposure the corresponding Ni(MVV) line changes its shape significantly, indicating formation of oxidized nickel. The consistent lowering of the enhanced T_C with exposure can be attributed to oxygen-induced gradual quenching of Ni atom magnetic moments that leads ultimately to full suppression of the surface ferromagnetic order. Quenching of Ni magnetic moment by adsorbed oxygen has been observed for the (111) surface by magnetometry [21], and predicted by electronic structure calculations for reconstructed O $p(2 \times 1)$ /Ni(110) [22] and for O chemisorbed on small Ni clusters [23]. Reductions in surface Curie temperatures by surface contamination have been reported for Gd(0001) [6] and Ni–20% Fe films [24]. Referring

finally to the Ar bombardment effects described above, such impinging ions are known to produce structural roughness at the near surface region that intensifies with increasing ion energy. The resultant gradual decrease of the enhanced T_C [Fig. 3(b)] is in qualitative agreement with trends predicted by effective-field theory for surface amorphization effects on T_C^s of Ising ferromagnet, which involves a parameter describing the amount of fluctuations in the exchange interactions due to geometric disorder [25]. Clearly, the remarkable effects of ion bombardment presented here, reflect and confirm the surficial origin of the enhanced magnetic transitions, and to our knowledge this is the first experimental evidence for such effects on Curie temperature.

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