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Invar behavior of fcc $Fe_{1-x}Ni_x$ thin films

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From measurements of the thermal expansion and magnetization on uhv evaporated fcc Fe-Ni alloy films we show that the deviation of the average magnetic moment from the Slater-Pauling curve, observed in Fe-Ni bulk alloys around $Fe_{65}Ni_{35}$, is not a necessary condition for the occurrence of the Invar effect. The results also address the long-debated issue of why in bulk Invar alloys the spin-wave stiffness is high when determined by inelastic neutron scattering, but low when a Bloch law is fitted to the low-temperature magnetization dependence.

Long debated in the history of the Invar effect[1] is the question of whether or not the deviation of the average magnetic moment from the Slater-Pauling curve observed in Fe-Ni alloys around the composition $Fe_{65}Ni_{35}$ is an Invar relevant feature, since this deviation does not occur in ordered Fe_3Pt Invar. Recently, it has been suggested from theoretical arguments that the specific properties of Invar are due to moment-volume instabilities, inherent to both Invar alloys Fe_3Ni and Fe_3Pt.[2–4] The physical nature of the Invar effect in both systems is therefore the same.

In the present investigation we give direct experimental proof for the correctness of this statement from measurements of the magnetization and thermal expansion of fcc Fe-Ni films with compositions in the Invar range. Our results also shed light on a second, historic puzzle of Invar. So far there has been no conclusive answer to the question of why the spin-wave stiffness constant of bulk $Fe_{65}Ni_{35}$ is as high as $D_{sw}=140$ meV Å^2, when determined by inelastic neutron scattering (INS), but as low as $D_m=60$ meV Å^2, when deduced from low temperature magnetization.[5] The difference has led to the statement[6] that in Invar some "hidden" excitations might exist which are not sensed by neutrons, but contribute to the magnetization. Our results on the films will show that in Fe-Ni Invar additional excitations result from nonpropagating longitudinal fluctuations, which are of structural origin.

$Fe_{1-x}Ni_x$ films ($0.34\le x\le 0.50$) are prepared in an uhv system ($p=2\times10^{-10}$ mbar) by simultaneously evaporating Fe and Ni from two independently monitored electron guns onto quartz substrates at room temperature (RT). To yield $Fe_{1-x}Ni_x$ films with fcc structure, a thin $Fe_{55}Ni_{45}$ layer (thickness $t=20$ nm) is evaporated prior to the deposition of the alloy films ($t=200$ nm). The precoating stabilizes the fcc phase since $Fe_{55}Ni_{45}$ has about the same lattice constant as $Fe_{65}Ni_{35}$, but in the structural phase diagram lies far from the γ-α (fcc-bcc) phase boundary.[1] The magnetization of the films is measured in the saturation field $H_s=530$ G between 4.2 and 900 K. The thermal expansion is determined with an x-ray spectrometer (Co $K\alpha$ radiation; $\lambda=1.7902$ Å) in the temperature range 100 to 350 K. The morphology of the films is investigated by transmission electron microscopy (TEM) at RT.

As a result of a "checking" experiment we show in Fig. 1 the x-ray scans at different temperatures for a pure fcc Au film ($t=100$ nm) directly evaporated onto a quartz substrate at RT. The (200)-peak position corresponds to a lattice constant $a_{RT}=4.084\pm0.005$ Å, in good agreement with the value for bulk Au ($a_{RT}=4.079$ Å).[7] As the temperature is lowered the peak shifts to larger scattering angles, reaching a lattice constant of $a=4.072$ Å for $T=100$ K. From the data we determine an average thermal expansion coefficient for the Au film $\alpha=(1/a)(\Delta a/\Delta T)=(16\pm1)\times10^{-6}$ K^{-1}, which is close to the bulk value ($\alpha=14.3\times10^{-6}$ K^{-1}), showing that the film expands independently of the substrate.

Figure 2 shows the x-ray intensity versus scattering angle at different temperatures of an fcc $Fe_{65}Ni_{35}$ film ($t=200$ nm) condensed at RT ("as prepared" state). The (111) peak around $2\Theta\simeq51.2°$ corresponds to a lattice constant of $a_{RT}=3.589\pm0.005$ Å, slightly lower as compared to $a_{RT}=3.593$ Å for bulk $Fe_{65}Ni_{35}$.[7] The (111) peak hardly changes position with temperature. From the data we find the average thermal expansion coefficient of the fcc $Fe_{65}Ni_{35}$ film $\alpha\le2\times10^{-6}$ K^{-1} in the range 100–350 K. This means that the film in Fig. 2 shows the Invar effect like the respective bulk. Similar results have been obtained for $Fe_{1-x}Ni_x$ films with $0.31\le x\le0.39$. The relatively large half widths of the (111) peaks in Fig. 2 [as well as (200) in Fig. 1] are caused by the small grain size of about 10–15 nm, in good agreement with the results from TEM investigations on the same films. Note that the half widths do not change, when the samples are cooled, i.e., strain is not induced during cooling.

In Fig. 3 we present the results of the magnetization measurements of the $Fe_{65}Ni_{35}$ film in the "as-prepared" state and after heating to $\sim$900 K ("annealed state"). Note the high value of the saturation magnetization at 0 K $M_s(0)=195$ emu/g and high Curie temperature $T_c\simeq700$ K in the "as-prepared" state, as compared to $M_s(0)=164$ emu/g and $T_c=520$ K in the "annealed" state. The latter values are close to those of the respective bulk. The inset of Fig. 3 clearly reveals that $M_s(0)$ (the contribution from the sublayer is subtracted) of all "as-prepared" films in the Invar range lies close or even above the Slater-Pauling curve, but drops into the region of the bulk (full curve) when the films are annealed. If we assume interdiffusion between the sublayer and the total bulk of the film, a small reduction of $M_s(0)$ of about 3% is expected to occur, which is for the present discussion of marginal importance. Figure 4 shows for the "annealed" $Fe_{65}Ni_{35}$ film that the Invar behavior is maintained, as is expected from the respective bulk. The half widths of the (111) peaks are reduced (average grain diameter ≈ 150 nm) due to grain growth and partial recrystallization. The lattice constant ($a_{RT} = 3.606$ Å) is slightly enhanced (0.5%) as compared to the "as-prepared" state.

We can thus summarize and emphasize: RT evaporated fcc $Fe_{1-x}Ni_x$ films with $0.31 \leq x \leq 0.39$ show high saturation magnetization $M_s(0)$ (close to the Slater-Pauling curve) and high Curie temperatures T_c, in contrast to the respective bulk material. After annealing of the films $M_s(0)$ and T_c drop to values comparable to the respective bulk. However, irrespective of the values of $M_s(0)$ and T_c the films show Invar behavior. We have thus experimentally proven that the deviation of the average magnetic

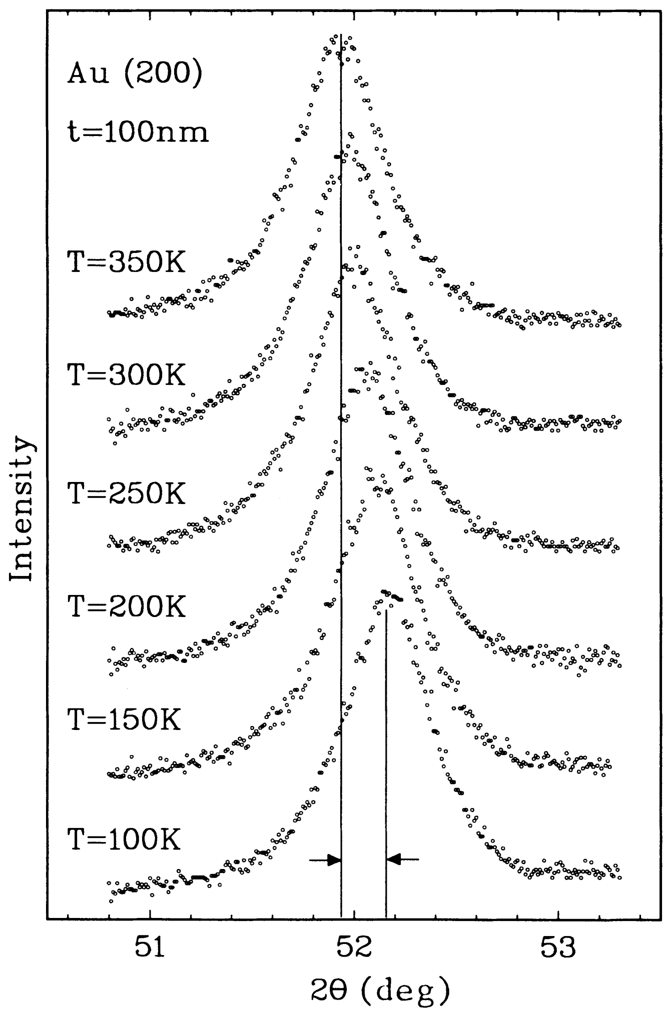

FIG. 1. X-ray spectrum at different temperatures for a pure Au film evaporated at RT.

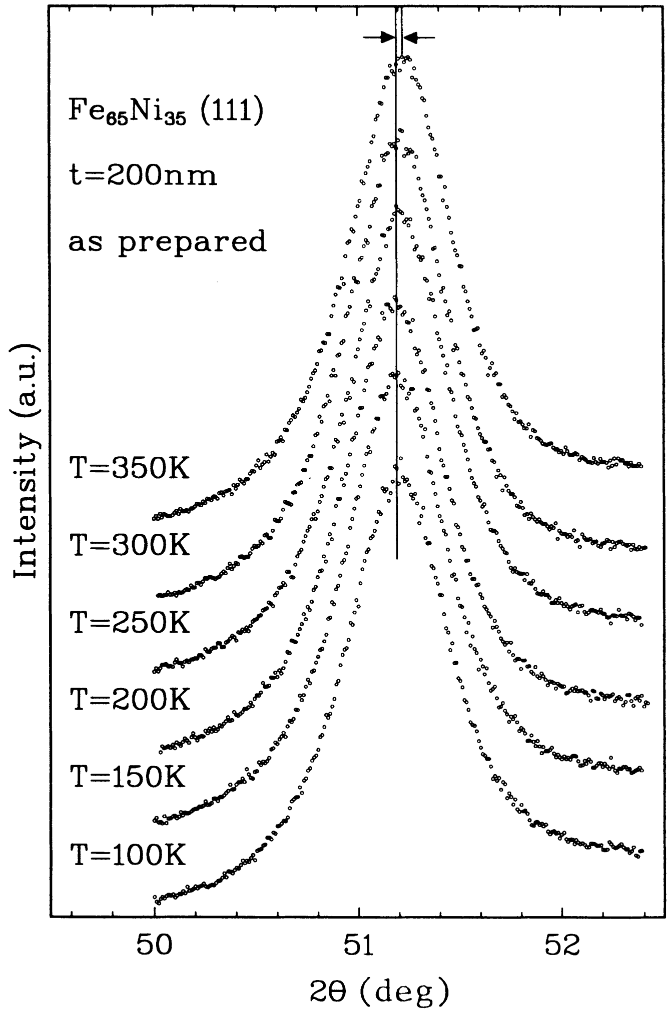

FIG. 2. X-ray spectrum at different temperatures for an fcc $Fe_{65}Ni_{35}$ film evaporated at RT ("as-prepared" state).

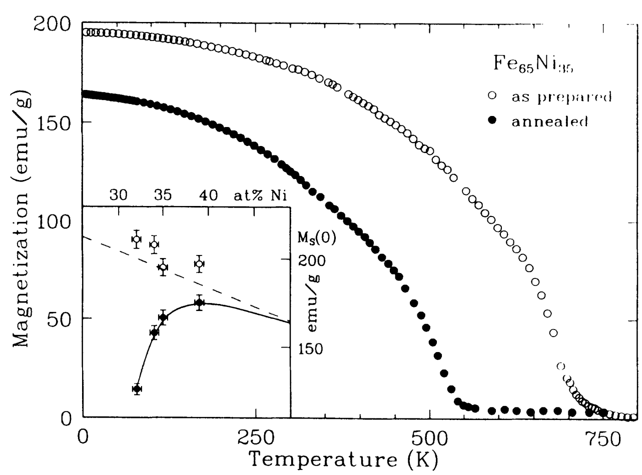

FIG. 3. Magnetization vs temperature for the fcc $Fe_{65}Ni_{35}$ film. Note the decrease in $M_s(0)$ and T_c after annealing. Inset: Slater-Pauling curve for bulk Fe-Ni (solid line); $M_s(0)$ of "as-prepared" films (open dots); $M_s(0)$ of "annealed" films (solid dots).

moment from the Slater-Pauling curve is not a necessary condition for the occurrence of the Invar effect.

The explanation of these observations on the basis of structural arguments is straightforward. Firstly, changes in the lattice constants cannot be the reason, since the lattice constants of the "as-prepared" as well as the "annealed" films deviate only $\pm 0.5\%$ from those of the respective bulk. Theoretical calculations[2–4] and a recent analysis of experimental data have shown[8] that an increase (reduction) of the lattice constant by $\pm 0.5\%$ leads to an increase (decrease) of the Fe moment by roughly $\pm 5\%$. Thus the experimentally observed variation of the lattice constants cannot explain a reduction of $M_s(0)$ of about 20% as we find for the annealed films (Fig. 3). Secondly, though bulk Fe-Ni and (Fe-Pt) Invar alloys do not undergo an fcc-bcc (γ-α) martensitic transition[8] they experience the so-called "premartensitic" transition[9] as a precursor to the martensite. Thirdly, it is well known that in bulk Fe-Ni Invar at low T antiferromagnetic (AF) Fe-Fe short-range order (SRO) and even AF γ-Fe precipitations do occur, around which there are regions with canted spins, forming spin-glass-like transition regions in the otherwise collinear FM Fe-Ni matrix.[10] We think that these spin-glass-like regions originate from the premartensitic transformation and mention in this context a recent model by Kartha et al.,[11] where premartensite has been discussed within a spin-glass model. These mixed magnetic regions are absent in the "as-prepared" Fe-Ni films as proven by the high values of $M_s(0)$ and T_c. This is because the premartensitic transition in these Fe-Ni films is prevented because of the small grain size, as in the rapidly quenched and consequently small-grained bulk Fe-Ni.[12] Further support stems from Mössbauer measurements on Fe-Ni films[13] which clearly have revealed that in the "as-prepared" state the hyperfine field (HF) distributions are sharp and purely ferromagnetic. After annealing, however, AF couplings do occur as indicated by a considerable low field contribution in the HF-distribution curve, as in bulk Fe-Ni Invar. AF couplings lead to the observed reduction of $M_s(0)$.[14]

The AF SRO also leads to the weak temperature dependence $M_s(T)$, characterized by small values of the spin-wave stiffness D_m, if a Bloch $T^{3/2}$ law is fitted to the data. This is shown in Fig. 5, where the reduced low temperature magnetization $M_s(T)/M_s(0)$ is plotted versus T for the $Fe_{65}Ni_{35}$ film in both states, bulk $Fe_{65}Ni_{35}$ as well as bulk $Fe_{50}Ni_{50}$ (both from Ref. 15). The curves give the respective fits to a $T^{3/2}$ law from which the D_m values of the film are determined. Omitted for clearness in Fig. 5 are the magnetization curves of an $Fe_{50}Ni_{50}$ film in both states, because $M_s(T)$ of this film renormalizes in almost the same fashion as the bulk material. The spin-wave stiffnesses for the film are $D_m = 220$ meV Å^2 ("as prepared") and $D_m = 215$ meV Å^2 ("annealed"). For the bulk the values are $D_m = 220$ meV Å^2 (Ref. 15) and $D_{sw} = 225$ meV Å^2 as determined from INS.[5] Thus all stiffnesses are about equal. The reason is that neither the film (in both states) nor the respective bulk contain any premartensite (AF SRO), because the composition $Fe_{50}Ni_{50}$ lies far from the γ-α transition boundary. Free of AF SRO is also the "as-prepared"

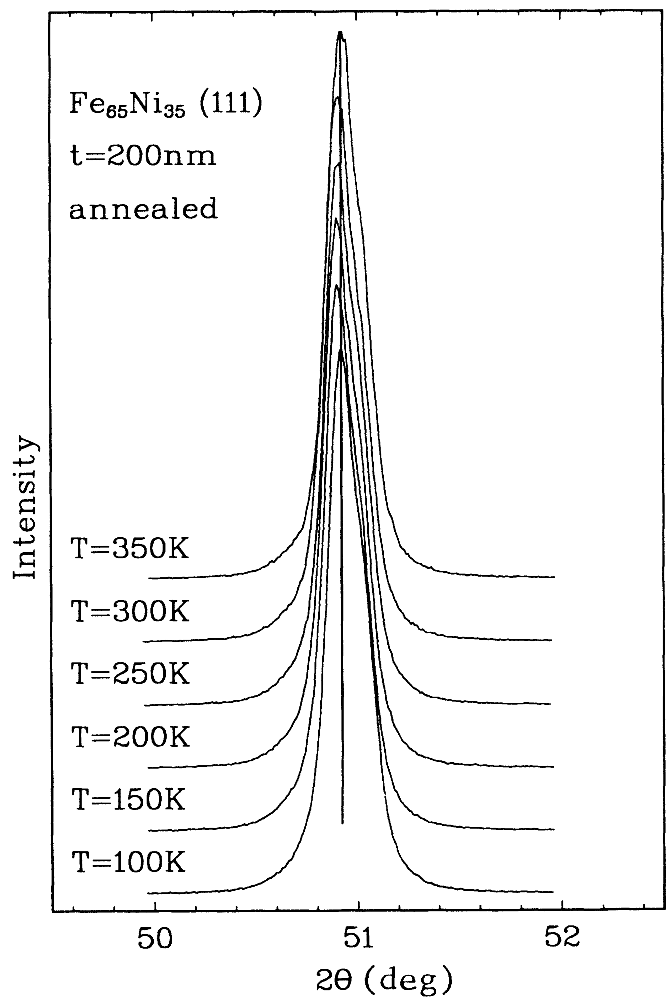

FIG. 4. X-ray spectrum at different temperatures for the same $Fe_{65}Ni_{35}$ film as in Fig. 2 after annealing to 900 K.

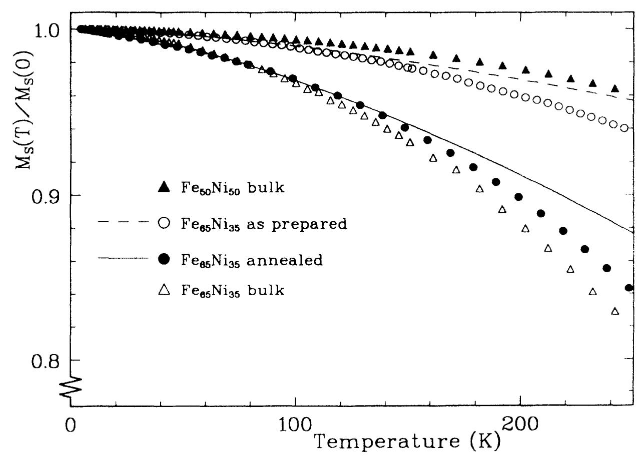

FIG. 5. Reduced magnetization $M_s(T)/M_s(0)$ vs temperature for the $Fe_{65}Ni_{35}$ film "as prepared" (open dots) and "annealed" (solid dots) together with respective fits to a Bloch law (curves). Data for bulk $Fe_{65}Ni_{35}$ (open triangles) and bulk $Fe_{50}Ni_{50}$ (solid triangles) both from Ref. 15.

$Fe_{65}Ni_{35}$ Invar film for which we find from Fig. 5 $D_m = 130 \pm 5$ meV Å^2. This value lies close to $D_{sw} = 140$ meV Å^2 as found from INS on bulk $Fe_{65}Ni_{35}$.[5] On the other hand, the "annealed" $Fe_{65}Ni_{35}$ film shows "weak" magnetic behavior with $D_m = 77 \pm 5$ meV Å^2, a value which compares well with bulk $Fe_{65}Ni_{35}$, $D_m = 60$ meV Å^2 as Fig. 5 exhibits. Both the annealed $Fe_{65}Ni_{35}$ film and the bulk incorporate the AF SRO caused by the premartensite as discussed above.

A second result thus stems from the present investigations. The long debated difference in spin-wave stiffness between INS and magnetization, specifically large for Fe-Ni Invar, is not a typical Invar feature. It is caused by a partial or premartensitic γ-α transformation leading to frustrated ("canted") spins in the otherwise ferromagnetic matrix. Why are these mixed magnetic contributions not sensed by the neutrons? A possible explanation stems from a theoretical investigation by Continentino and Rivier[16] for amorphous ferromagnets for which similar differences between D_m and D_{sw} have been observed. The authors show that spin canting in a (moderately) frustrated system causes longitudinal fluctuations with amplitudes as large as the transverse ones. These modes called "diffusions" do not propagate but result in an additional $T^{3/2}$ term in the low temperature magnetization. In the INS spectra these longitudinal fluctuations show up as a broad central peak, which is indeed observed for Fe-Ni Invar.[5]

Note that a $T^{3/2}$ dependence in Fe-Ni is only found at low temperatures (cf. Fig. 5), and another contribution seems to be necessary to fully describe the $M(T)$ behavior of Invar. In this context the existence of magnetoacoustic modes, with a strong coupling of the magnetic and lattice degrees of freedom, has recently been discussed and demonstrated in polarized-neutron experiments on $Fe_{65}Ni_{35}$.[17] In which way these magnetoacoustic modes ("elastomagnons") contribute to the magnetization is unknown at present. Our investigations could therefore stimulate finite-temperature calculations within the fixed-spin moment method,[2–4] which successfully so far only give a general picture for the moment-volume-instabilities at zero K. Moreover, similar experimental investigations are presently undertaken on Fe-Pt films to support our findings that Invar is a general property of 3d alloys and it is unnecessary to distinguish between soft magnetic Fe-Ni type and hard magnetic Fe-Pt-type Invar.

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