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# The magnetic properties across the martensitic transition in the $Co_{38}Ni_{34}Al_{28}$ alloy

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ABSTRACT

The magnetic properties of the $Co_{38}Ni_{34}Al_{28}$ alloy have been studied. The alloy exhibits a first order austenite–martensite phase transition in the temperature region between 155 and 247 K. A strain of 0.07% is produced across this phase transition. The Arrott plots obtained from the isothermal magnetic field dependence of magnetization indicate the presence of spontaneous magnetization both in the austenite and martensite phases, confirming the ferromagnetic character of the alloy up to room temperature. The temperature dependence of the high field magnetization indicates the presence of spin wave excitations, spin wave excitation gap and spin wave–spin wave interactions in the martensite phase. The magnetic anisotropy energy constant for the $Co_{38}Ni_{34}Al_{28}$ alloy is estimated both with the help of the standard law of approach to saturation of magnetization, and also from the field dependence of magnetization using the field for technical saturation of magnetization. The temperature dependences of these energy terms are compared. The estimated values of the magnetic anisotropy constant seem to be in agreement with the magnitude of the spin wave excitation gap estimated from the temperature dependence of high field magnetization.



## 1. Introduction

The recent interest in research on the off-stoichiometric Ni–Co–Al based alloys is because of their potential as ferromagnetic shape memory materials [1–5]. Earlier, the NiAl based systems came into focus with the discovery of shape memory effect in the paramagnetic NiAl–β phase by Enami and Nenno [6]. With the addition of Co in the NiAl alloys, a new class of alloys emerged in which the β phase martensitically transforms into a $\beta'(L1_0)$ structure. Depending on the concentration of Ni and Co and varying annealing conditions, a γ (A1 structure) or γ′ ($Ni_3Al$, $L1_2$ structure) phase having different mechanical properties can be precipitated in the alloys [7]. The introduction of γ-phase incorporates ductility in the otherwise brittle β-phase Co–Ni–Al alloy, making the alloy more machinable. Oikawa et al. [1] have reported the composition dependence of the Curie temperature ($T_c$), and the martensite start and austenite finish temperatures in the $Ni_{71-x}Co_xAl_{29}$ alloy. With a slight change in Co concentration, the magnetic state of the high temperature austenite phase and the low temperature martensite phase can be chosen to be either paramagnetic or ferromagnetic in character. Chatterjee et al. have studied the temperature dependent magnetic and structural properties for different Co–Ni–Al alloys across the martensitic transition [8]. Apart from the dependence on composition, the martensite start and austenite finish transition temperatures also depend strongly on the annealing conditions [9,10]. Tanaka et al. [9] extensively studied the dependence of the martensitic and magnetic phase transitions on the annealing conditions. The Curie temperature and the martensite start temperature increases with increasing annealing temperature for the $Co_{38}Ni_{34}Al_{28}$ alloy due to the variation of chemical composition of the β and γ phases. However, to the best of our knowledge, a detailed understanding of the magnetic properties of the $Co_{38}Ni_{34}Al_{28}$ alloy across the martensitic transition has not yet evolved.

In the present work, we have studied in detail the magnetic properties across the martensitic transition in the $Co_{38}Ni_{34}Al_{28}$ alloy. This particular composition was chosen because as per the compositional phase diagram of the Ni–Co–Al alloys reported by Oikawa et al. [1] this composition is expected to be a ferromagnetic shape memory alloy with ferromagnetic austenite and martensite phases. We have found that a strain of 0.07% is produced across this phase transition. The magnetization results confirm the ferromagnetic character of the alloy up to room temperature. The nature of the magnetic excitations in the martensite phase and the magnetic anisotropy in the martensite and austenite phases of the alloy is studied, which reveals interesting features that could be useful the for future application of this alloy system.

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## 2. Experimental details

A polycrystalline sample with the nominal composition $Co_{38}Ni_{34}Al_{28}$ was prepared using high purity elements in an arc melting furnace in an inert argon atmosphere. The sample was flipped and re-melted several times to ensure the homogeneity. The sample was then sealed in a quartz ampoule in argon atmosphere, and was annealed at 1275 °C for 24 h followed by quenching in ice water to introduce the γ phase in the otherwise brittle β phase [9]. Structural characterization of the alloy was done with the help of X-ray diffraction (XRD) study performed in a PANalitical X'Pert PRO MRD machine, using Cu Kα radiation ($\lambda=1.54056$ Å). The XRD results indicate the presence of both β (approximately 40%) and γ (approximately 60%) phases in the sample. The β phase has a bcc (B2) structure with a lattice parameter of 2.86 Å, and the γ phase has an FCC (A1) structure with a lattice parameter of 3.575 Å. Only the β-phase undergoes a transition from the cubic austenite phase to the tetragonal martensite β′-phase, whereas γ phase remains unchanged and does not play any role in the martensitic transition. There was no indication of the martensite β′($L1_0$) phase from the XRD pattern at room temperature. The electrical resistivity of the sample as a function of temperature was measured between 350 K and 77 K, using the standard four probe technique in a homemade liquid nitrogen cryostat. DC magnetization ($M$) as a function of temperature ($T$) and applied magnetic field ($H$) was measured using a SQUID magnetometer (MPMS-XL, Quantum design) and a vibrating sample magnetometer (VSM, Quantum Design). Strain measurement as a function of temperature was performed between 350 K and 77 K using the strain gage technique [11]. In this measurement the relative change in length $\Delta L/L$ was measured using a differential method, keeping copper as the reference material, and the length at 293 K as the reference length. The temperature dependence of strain is thus expressed in terms of $\Delta L/L_{293}$ where $L_{293}$ is the length of the sample at 293 K.

## 3. Results and discussion

Fig. 1(a) shows the temperature dependence of the normalized electrical resistivity of the $Co_{38}Ni_{34}Al_{28}$ alloy as a function of temperature. While cooling down the sample from room temperature, resistivity first decreases nearly linearly as is normally expected in a metal. But below 210 K, it increases sharply before exhibiting the near-linear temperature dependence again below 150 K. While warming up, the sample exhibits a similar temperature dependence of electrical resistivity along with a distinct thermal hysteresis associated with the sharp drop in the magnitude of resistivity. Thermal hysteresis in an experimental observable is a signature of a first order phase transition [12]. The Co–Ni–Al alloy system is known to exhibit a first order austenite–martensite phase transition with varying temperature [13]. The large change in resistivity along with the associated thermal hysteresis observed in Fig. 1(a) is therefore attributed to the first order austenite–martensite phase transition in the present $Co_{38}Ni_{34}Al_{28}$ alloy. The martensite start and the austenite start temperature are located from the change in the curvature of the resistivity vs. temperature curves using the first order derivatives of these curves. The martensite start and the austenite start temperature are found to be 224 and 171 K, respectively. The martensite finish temperature is defined as the point of convergence of the heating and cooling curves on low temperature side (the limit of supercooling [12] of the austenite phase). This temperature is found to be 155 K. The resistivity vs. temperature curves for heating and cooling for the present $Co_{38}Ni_{34}Al_{28}$ alloy do not converge on the high temperature side making the austenite finish temperature difficult to determine. This non-convergence is related to the fact that the resistivity of the alloy keeps increasing every time it is taken through a heating-and-cooling cycle across the martensitic transition. However, as an approximation the austenite finish temperature is taken as the temperature from where the heating and the cooling curves becomes parallel and this comes out to be 247 K.

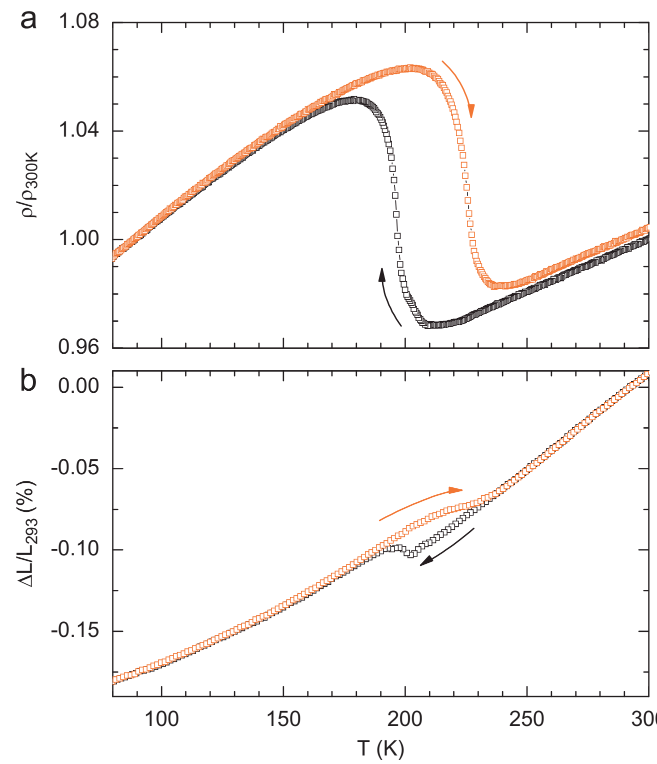


**Fig. 1.** (a) Normalized electrical resistivity and (b) strain as a function of temperature of the $Co_{38}Ni_{34}Al_{28}$ alloy.

Fig. 1(b) shows the temperature dependence of the strain ($\Delta L/L_{293}$) in the $Co_{38}Ni_{34}Al_{28}$ alloy. Starting from well inside the austenite phase, the strain decreases with the decrease in temperature, shows a sharp step-like feature starting at 203 K and then decreases continuously with further decrease in temperature. Similar behavior is also observed in the warming-up cycle, along with a thermal hysteresis associated with the step-like feature mentioned above. The step in the warming-up cycle is broader and less sharp as compared with the cooling down cycle. The step-like feature in the temperature dependence of strain and the associated thermal hysteresis is attributed to the austenite–martensite phase transition in the alloy. The characteristic temperatures for this phase transition obtained from the temperature dependence of strain by following a similar procedure as done for resistivity are: martensite start temperature = 210 K; martensite finish temperature = 170 K; austenite start temperature = 177 K and austenite finish temperature = 240 K. These temperatures match reasonably well with those obtained from the resistivity measurements. A change of strain of about 0.07% is observed across the austenite–martensite phase transition. However, this change of strain is less than that observed by Wang et al. who measured a strain of 0.15% across this phase transition in $Co_{39}Ni_{33}Al_{28}$ ribbons [14].

Fig. 2 shows the dc-magnetization of the $Co_{38}Ni_{34}Al_{28}$ sample as a function of temperature in zero-field cooling (ZFC), field cooled cooling (FCC) and field cooled warming (FCW) protocols in the presence of 100 Oe and 50 kOe applied magnetic fields. In the ZFC protocol the sample is cooled down to 5 K in zero magnetic field and then the measurement is performed in the desired field