The Phase Relations of the Co-Ni-In Ternary System at 673 K and 873 K and Magnetic Properties of Their Compounds

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Abstract: The phase relationships of the ternary Co-Ni-In system at 673 K and 873 K were investigated by means of powder X-ray diffraction, scanning electron microscopy equipped with energy dispersive spectroscopy, and optical microscopy. Though CoIn₂ does not exist at 873 K, the ternary solid solution Co₁₋ₓNiₓIn₂ exists at both 673 K and 873 K with different composition ranges. The Rietveld refinements were carried out to investigate the crystal structure of Co₁₋ₓNiₓIn₂ (x = 0.540, and 0.580) and Ni₂₋ₓCoₓIn₃ (x = 0.200). The magnetization dependence of temperature (MT) curves of Ni₂₋ₓCoₓIn₃ (x = 0.200) and Co₁₋ₓNiₓIn₂ (x = 0.540) are similar to those of the ferromagnetic shape memory alloys Ni-Mn-A (A = Ga, Sn, and In), but do not undergo martensitic transformation. The maximum magnetic entropy changes in Ni₂₋ₓCoₓIn₃ (x = 0.200) and Co₁₋ₓNiₓIn₂ (x = 0.540) under 3T are 1.25 and 1.475 J kg⁻¹ K⁻¹, respectively.

Keywords: Co-Ni-In; phase diagram; X-ray diffraction; magnetic properties

1. Introduction

Recently, Ni-Mn-In has drawn increasing attention due to its fascinating multifunctional properties including its shape memory effect [1], magnetocaloric effect [2], elastocaloric effect [3], magnetothermal conductivity [4], magnetic superelasticity [5], barocaloric effect [6], and large exchange bias effect [7] associated with the martensitic-type phase transformation. A large number of researches have shown that the properties of the Ni-Mn-In alloys have been highly improved when accompanied with a small amount of Co doping into Ni-Mn-In ternary compounds [8–10]. This brings more attention to the Ni-Co-Mn-In quaternary compounds and another upsurge of research of the alloys [11–14]. The martensitic transformation, which belongs to first-order magnetostructural transformation, led to a large magnetic entropy change (ΔS) which makes Ni-Co-Mn-In alloys promising candidates for magnetic refrigeration materials [15–17]. A giant magnetocaloric effect driven by structural transitions was found in Ni₄₅.₇Mn₃₆.₃In₁₃Co₅, which resulted in a high adiabatic temperature change (ΔTad) of ~6.2 K under a low field of 2T [2]. In Cheng’s work, the temperature-induced martensitic transformation of Ni₄₂Co₈Mn₇₇In₁₂₅ alloy achieved a giant (ΔS̄) of 14.30 J·K⁻¹·kg⁻¹ and refrigeration capacity (RC) up to 549 J K⁻¹. Additionally, the near-room-temperature working temperature range

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of 248–295 K makes it superior among a number of reported magnetocaloric materials [18]. Large magnetic field-induced martensitic transformation led to enormous recoverable deformation, which can be easily observed in Ni-Co-Mn-In alloys, making it an attractive shape memory functional material [19–21]. Stresses of over 100 MPa were generated in Ni$_{45}$Co$_{5}$Mn$_{36.7}$In$_{13.3}$ on the field of 7 T. 3% deformation, and full recovery of the original shape was discovered as a result of magnetic field-induced strains [1]. After sintering at 873 K, Ni$_{45}$Mn$_{36.4}$In$_{13.4}$Co$_{5}$ showed an almost perfect shape memory effect in which martensitic transformation played the dominant role, since the shape recovery was as high as 11.4% [22]. With such excellent magnetocaloric and shape memory properties, they can extensively serve society. However, large thermal transformation hysteresis, needing a high-driving magnetic field and poor mechanical properties, severely hinders their commercialization [10,23,24]. Phase diagrams are important for designing and preparing of Ni-Co-Mn-In alloys with potentially excellent properties. In addition, they enable the exploration of new functional materials. Only the phase diagrams of the Ni-Mn-In and Ni-Co-Mn ternary systems among the four sub-ternary systems of the Ni-Co-Mn-In quaternary system have been studied [25–28], while the phase diagrams of the other systems are not available in literature. At the same time, investigation on the magnetic properties of the compounds in these three ternary systems also plays a significant role in exploring new potential magnetic materials, such as refrigeration materials. This paper will focus on one of the four sub-ternary systems of the Ni-Co-Mn-In quaternary system, the Co-Ni-In system, and the magnetic properties of its compounds.

The phase diagrams of the binary systems Co-Ni, Co-In, and Ni-In related to the Ni-Co-In ternary system have been studied [29–31]. According to the Co-Ni binary phase diagram, there is no intermediate phase in this system. Co and Ni form an infinite solid solution that exists in the form of α-(CoNi) (space group: Fm$\overline{3}$m) above 695 K. Below 695 K, the alloys are in a ε-(CoNi) hexagonal phase (Space group P6$_3$/mm) at a low nickel content range. With the increase in Ni content, the ε-Co→α-Co transformation occurs. Two binary compounds, CoIn$_2$ and CoIn$_3$, exist in the Co-In binary system, and the compounds are formed by peritectic reactions of α-Co + L → CoIn$_2$ (823 K) and CoIn$_2$ + L→ CoIn$_3$ (763 K), respectively. The binary system undergoes a monotectic reaction at 1559 K. The composition of the monotectic is about 77 at.% In.

There are seven binary compounds, i.e., Ni$_3$In, Ni$_2$In, ζ, Ni$_{13}$In$_9$, NiIn, δ, Ni$_2$In$_3$, and Ni$_3$In$_7$ in the Ni-In binary system according to Ref. [31]. Intermetallic compounds of Ni$_3$In, Ni$_2$In, NiIn, Ni$_2$In$_3$, and Ni$_3$In$_7$ are stoichiometrically determined. The ζ phase is stable from 755 to 1223 K with a maximum range from 31.2 to 40.5 at.% In, and the compound Ni$_{13}$In$_9$ has a composition range of 38.0–41.0 at.% In, and the compound Ni$_{13}$In$_9$ have a composition range of 38.0–41.0 at.% In. Additionally, the δ phase forming at higher temperature is stable in the temperature range of 1043–1203 K and has a composition range of 52–58.2 at.% In. The solid solubility of In in Ni increases with temperature, which increases from 3.3 to 13.4 at.% In when temperature increases from 693 to 1181 K. No solubility of Ni in In has been reported. A ternary compound, Ni$_2$CoIn, was investigated theoretically by first principles in [32], showing that the compound crystallized in a cubic structure with a space group of Fm$\overline{3}$m and lattice parameter a = 0.5944 nm. The Ni atom occupies the 8c (0.25, 0.25, 0.25) site, Co occupies the 4b (0.5, 0.5, 0.5) site, and the In atom occupies the 4a (0, 0, 0) site. Calculation of formation energy indicates the instability of the austenitic structure in Ni$_2$CoIn and a strong tendency of martensitic transformation. Table 1 shows the crystallographic data of the compounds in the Co-Ni-In system.
### Table 1. Crystallographic data of the compounds in the Co-Ni-In system.

| Compounds   | Structure Type | Space Group | Lattice Parameters (nm) | References |
|--------------|----------------|-------------|-------------------------|------------|
| CoIn₂       | CuMg₂          | Fddd        | a: 0.5282, b: 0.5282, c: 1.7846, β: 90° | [30]       |
| CoIn₃       | Mg             | P6₃/mmc     | a: 0.6829, b: 0.6829, c: 0.7094, β: 90° | [30]       |
| Ni₂In       | W              | Im₃m        | a: 0.2929, b: 0.2929, c: 0.2929, β: 90° | [33]       |
| Ni₃In       | Ni₃Sn          | P6₃/mmc     | a: 0.5320, b: 0.5320, c: 0.4242, β: 90° | [31]       |
| Ni₃In       | AuCu₃          | Pn₃m        | a: 0.3750, b: 0.3750, c: 0.3750, β: 90° | [31]       |
| Ni₂In       | Ni₂In          | Pn₃m        | a: 0.4179, b: 0.4179, c: 0.5131, β: 90° | [31]       |
| Ni₃In₉     | Ni₃In₉         | C2/m        | a: 1.4646, b: 0.8329, c: 0.8977, β: 35.35° | [31]       |
| Ni₃In₇     | AsNi           | P6₃/mmc     | a: 0.4178, b: 0.4178, c: 0.5137, β: 90° | [33]       |
| Ni₃In      | CoSn           | P6₃/mmc     | a: 0.5243, b: 0.5243, c: 0.4342, β: 90° | [31]       |
| Ni₃In      | CsCl           | Pn₃m        | a: 0.3092, b: 0.3092, c: 0.3092, β: 90° | [31]       |
| Ni₃In₃     | Al₃Ni₂         | P₃m1        | a: 0.4930, b: 0.4930, c: 0.5201, β: 90° | [31]       |
| Ni₃In₇     | Cu₃Zn₈        | I₄₃m        | a: 0.9180, b: 0.9180, c: 0.9180, β: 90° | [33]       |
| Ni₂CoIn    | BiF₃          | Fm₃m        | a: 0.5944, b: 0.5944, c: 0.5944, β: 90° | [32]       |

#### 2. Experimental

All samples with a mass of 2 g were prepared in an electric arc furnace under argon atmosphere. The purities of initial metals Co, Ni, and In were 99.9 wt. %, 99.99 wt. % and 99.9 wt. %, respectively. The material source is General Research Institute for Nonferrous Metals (Beijing, China). A proper amount of In was added to each samples due to the loss of In. Titanium was used as the oxygen scavenger during the melting process. The samples were melted three times for the purpose of homogeneity of the alloy samples. All the as-cast samples were sealed in evacuated quartz tubes to anneal at higher temperature for further homogenization. The In-rich (> 50 at.% In) alloys were kept at 923 K/673 K for 30 days, while the other alloys homogenized at 1073 K for 20 days. After homogenization annealing, the samples used for the 873 K section were cooled down to 873 K with a cooling rate of 50 K/day and maintained at 873 K for 20 days to reach equilibrium, while those used for the 673 K section were cooled down to 673 K and maintained at 673 K for 20 days. Finally, all the samples were quenched into ice-water mixture.

The X-ray powder diffraction (XRD) data of the Co-Ni-In alloy samples were obtained by using a Rigaku D/max 2500 V powder diffractometer (Cu Kα1 radiation, λ = 1.54060 Å; Tokyo, Japan). The powder XRD data for phase analysis were collected in a continuous scanning mode, and those for Rietveld refinement were collected in a step scanned mode with a step size of 0.02°. The high temperature XRD data were collected by using a Bruker D8 advance diffractometer. The Rietveld refinements for some selected samples were carried out by using FullProf programs [34,35]. Scanning electron microscopy (SEM, Hitachi S-3400N or SU8000; Tokyo, Japan) and optical microscopy (Axio Imager A2m, Zeiss, Jena, Germany) were used for microstructure analysis, and energy dispersive analysis (EDS) was applied for the measurements of sample chemical and phase compositions. The samples used for SEM/EDS measurements were corroded with clear water. Magnetic measurements were carried out in the Physical Property Measurement System (PPMS, Quantum Design; San Diego, CA, USA).

#### 3. Results and Discussion

The phase analysis was performed on all the XRD data of the equilibrated Co-Ni-In samples with the aid of the Powder Diffraction File 2 (PDF2) database released by International Center for Diffraction Data (ICDD). The diffraction patterns of those compounds absent in the PDF2 database were calculated from the crystallographic data available in references. By carrying out the phase identification on the XRD patterns of each Co-Ni-In sample, the phase components of each sample were obtained. The selected samples were further observed by SEM/EDS and optical microscopy for phase identification and composition measurements.
3.1. Phase Analysis

3.1.1. Phase Analysis at 673 K

Table S1 shows the XRD and SEM/EDS analysis results of the selected Co-Ni-In samples at 673 K. The analysis on the XRD patterns of all the binary and ternary Co-Ni-In samples shows eight binary compounds, i.e., Ni3In, Ni2In, Ni13In7, Niln, Ni2In3, Ni3In7, Coln3, and Coln2, existing at 673 K. The binary compounds Ni4In and Ni13In7 were not observed in our experimental conditions. This is in good agreement with the Co-Ni, Co-In, and In-Ni binary phase diagrams. The Backscattered electrons (BSE) micrographs of the alloys No. 1 (Co10Ni75In15) and No. 2 (Co4Ni34In62) are shown in Figure 1a,b. Both alloys contain two phases. EDS analysis on alloy No. 24 (Co10Ni75In15) in Figure 1a revealed that the dark gray phase with composition of Co35.53(5)Ni62.15(4)In2.31(4) was identified as α-Ni Coα (x = 0.355), and the gray phase with composition of Co1.02(4)Ni72.26(5)In26.72(5) was Ni3In. In Figure 1b, for the sample No. 25 (Co4Ni34In62), the dark gray phase with composition of Co2.36(4)Ni59.12(3)In38.52(5) was verified to be Ni2−xCoxIn3 (x = 0.118), and the gray phase with composition of Co0.86(6)Ni32.43(5)In66.72(6) was Ni3In7. These results proved the existence of Ni3In, Ni2In3, and Ni3In7 at 673 K, which is in agreement with the literature [26,31].

![Figure 1. BSE micrograph of (a) No. 1 (Co10Ni75In15) and (b) No. 2 (Co4Ni34In62).](image)

In order to verify the existence of the ternary compound Ni2CoIn, which was investigated by using the first principle calculation as described by Bai et al. [35], a series of samples with compositions near Ni2CoIn was prepared. Figure 2 presents the XRD patterns of sample No. 3 (Co25Ni50In25), No. 4 (Co22Ni52In26), and No. 5 (Co27Ni48In25), and none of the XRD data of these samples correspond to the diffraction pattern calculated from the crystallographic data of Ni2CoIn as shown in the literature [35]. The XRD analysis on all of these alloys showed that these alloys contained the three phases of Ni13−xCo,In (x = 0.702), Ni1−xCo,In (x = 0.125), and α-Ni1−xCoα (x = 0.400) pointing to the absence of Ni2CoIn at 673 K. Figure 3a,b show the SEM micrographs of samples No. 5 and No. 6, respectively, as well as the composition of each phase obtained by EDS. The results also indicated that these two alloys contained the three phases of Ni13−xCo,In (x = 0.702), Ni1−xCo,In (x = 0.125) and α-Ni1−xCoα (x = 0.4), which proved the non-existence of Ni2CoIn at 673 K.
3.1.2. Phase Analysis at 873 K

Table S2 gives the XRD and SEM/EDS analysis results of the selected Co-Ni-In samples at 873 K. The analysis on the XRD patterns of all the binary and ternary Co-Ni-In samples shows that six binary compounds, i.e., Ni$_3$In, Ni$_2$In, Ni$_{13}$In$_9$, ξ, NiIn, and Co$_{1-x}$Ni$_x$In$_2$, exist at 873 K.

According to [12], a peritectic reaction L + (α) Co → CoIn$_2$ occurs at 823 K, and the compound CoIn$_2$ does not exist at 873 K. However, in the present work, a solid solution Co$_{1-x}$Ni$_x$In$_2$ was found at 873 K. The solid solution of Co$_{1-x}$Ni$_x$In$_2$ crystallized in the same crystal structure as that of CoIn$_2$. Figure 4a,b show the XRD pattern and SEM micrograph of alloy No. 26 (Co28Ni24In48). The XRD analysis result revealed that the alloy contained the three phases of Co$_{1-x}$Ni$_x$In$_2$ (x = 0.612), Ni$_2$–Co$_x$In$_3$ (x = 0.450), and α-Co$_{1-x}$Ni$_x$ (x = 0.200), as seen in Figure 4a. The composition measurement showed that the grey phase with composition of Co8.69(5)Ni32.99(4)In58.32(4), the light gray phase with composition of Co20.10(5)Ni16.82(6)In63.08(5), and the dark phase with composition of Co82.21(5)Ni17.16(6)In0.63(5) were identified to be the three phases of Ni$_2$–Co$_x$In$_3$ (x = 0.160), Co$_{1-x}$Ni$_x$In$_2$ (x = 0.612), and α-Co$_{1-x}$Ni$_x$ (x = 0.200), respectively, as seen in Figure 4b. Figure 5 shows the XRD pattern of alloy No. 27 (Co26Ni6In68). The XRD pattern in Figure 5 clearly indicates that the alloy contained the two phases of Co$_{1-x}$Ni$_x$In$_2$ and In, which confirmed Co$_{1-x}$Ni$_x$In$_2$ existed at 873 K once again. This suggests that the addition of Ni into CoIn$_2$ stabilized the compound and raised the temperature of the peritectic reaction L + (α) Co → Co$_{1-x}$Ni$_x$In$_2$. 

![Figure 2](image1.png)

**Figure 2.** XRD patterns of samples No. 3 (Co25Ni50In25), No. 4 (Co22Ni52In26), and No. 5 (Co27Ni48In25).

![Figure 3](image2.png)

**Figure 3.** BSE micrograph of samples (a) No. 3(Co25Ni50In25) and (b) No. 4 (Co22Ni52In26).
The XRD pattern and SEM micrograph of alloy No. 28 (Co8Ni22In70) are shown in Figure 6a,b, respectively. The XRD analysis of the alloy indicated that the three phases of Co$_{1-x}$Ni$_x$In$_2$ ($x = 0.612$), Ni$_{2-x}$Co$_x$In$_3$ ($x = 0.450$) and In (Liquid) coexisted in the alloy, and no diffraction patterns of Ni$_3$In$_7$ and/or CoIn$_3$ were observed. The SEM/EDS analysis on alloy No. 28 also gave the same results. This indicates that Ni$_3$In$_7$ and CoIn$_3$ do not exist at 873 K. Figure 7 shows the SEM micrograph of No. 29 (Co$_{18}$Ni$_{52}$In$_{30}$) alloy. It is clearly seen that the alloy is composed of three phases. EDS measurements showed that the gray phase with composition of Co$_{10.91(5)}$Ni$_{46.53(4)}$In$_{42.56(4)}$ was identified as Ni$_{13-x}$Co$_x$In$_2$ ($x = 2.634$), the dark gray phase with composition of Co$_{5.94(6)}$Ni$_{55.83(5)}$In$_{38.28(5)}$ was verified to be $\xi$, and the dark phase with composition of Co$_{48.69(4)}$Ni$_{49.12(4)}$In$_{2.19(3)}$ was $\alpha$-Ni$_{1-x}$Co$_x$ ($x = 0.500$). This result suggests that the $\xi$ phase existed at 873 K, which is similar to Schmutterer’s investigation [36].

Compared to the phases at 673 K, the binary compounds, i.e., Ni$_3$In, Ni$_2$In, Ni$_{13}$In$_9$, Niln, Ni$_2$In$_3$, and $\xi$, exist at 873 K, while the binary compounds Ni$_3$In$_7$, CoIn$_3$, and CoIn$_2$ disappeared at 873 K. Although CoIn$_2$ does not exist at 873 K, the ternary solid solution Co$_{1-x}$Ni$_x$In$_2$ exists at both of 673 K and 873 K with different composition ranges. No new binary and ternary compounds were found at 673 K and 873 K.
3.2. Solid Solubility

The solid solubilities of Co In Ni$_2$In, NiIn, Ni$_{13}$In$_9$, Ni$_2$In$_3$, and Ni, as well as Ni in CoIn$_2$ and Co at 673 K and 873 K were determined by XRD using the phase-disappearing and lattice parameter method combined with the SEM (EDS). The rough maximum solid solubility of above compounds was estimated by comparing the movement of the diffraction patterns of the single phases to the disappearance of the phases. A few series samples such as Ni$_{1-x}$Co$_x$In and Co$_{1-x}$Ni$_x$In$_2$ were prepared for the purpose of the solid solubility determination in the Co-Ni-In ternary system. The computer software Jade 5.0 was used to calculate and refine the lattice parameters of the samples Ni$_{1-x}$Co$_x$In and Co$_{1-x}$Ni$_x$In$_2$ from the XRD patterns.

3.2.1. Solid Solubility at 673 K

Figure 8 presents the XRD patterns of the samples Ni$_{1-x}$Co$_x$In ($x = 0.04, 0.08, 0.12, 0.14$) at 673 K. It can be clearly seen that these samples (except that of $x = 0.14$) contained the single phase of Ni$_{1-x}$Co$_x$In, pointing to the maximum solid solubility of Co in NiIn being between $x = 0.12$ and $x = 0.14$. Figure 9a,b show the variation in the lattice parameter $a$ and the lattice parameter $c$ of Ni$_{1-x}$Co$_x$In with the content of Co, which were calculated from the XRD patterns by Jade 5.0. It can be seen from
Figure 9a,b that the maximum solid solubility of Co in Ni1−xCo3In is \( x = 0.125 \) (6.25 at.% Co). Further analysis on the sample Ni1−xCo3In (\( x = 0.14 \)) by the SEM (EDS) also showed that the alloy contains the three phases of Ni1−xCo3In (\( x = 0.125 \)), Ni2−xCo3In3 (\( x = 0.400 \)), and \( \varepsilon \)-Co1−xNi8 (\( x = 0.280 \)), as seen in Figure 10, which is felt in a three-phase region. The composition measurement shows that the dark grey phase with composition of Co5.75(5)Ni45.02(6)In49.23(6) is Ni1−xCo3In (\( x = 0.125 \)), the grey phase with composition of Co7.82(4)Ni33.11(5)In58.07(5) is Ni2−xCo3In3 (\( x = 0.400 \)) and the dark phase with composition of Co72.81(7)Ni26.18(6)In1.01(5) is \( \varepsilon \)-Co1−xNi8 (\( x = 0.280 \)). This caused the maximum solid solubility of Co in Ni1−xCo3In to be 5.82 at.% Co at 673 K, and this value is similar to that obtained by the lattice parameter method, i.e., \( x = 0.125 \) (6.25 at.% Co). This further supports that the maximum solid solubility of Co in Ni1−xCo3In is 6.25 at.% Co at 673 K.

![Figure 8. XRD patterns of the sample Ni1−xCo3In (x = 0.04, 0.08, 0.12, 0.14).](image)

![Figure 9. Variation of (a) the lattice parameter a and (b) lattice parameter c of Ni1−xCo3In on Co content.](image)

![Figure 10. BSE micrograph of the sample Ni1−xCo3In (x = 0.14).](image)
Similarly, the maximum solid solubilities of Ni in Co$_{1-x}$Ni$_x$In$_2$ and ε-Co$_{1-x}$Ni$_x$ were determined to be 18.64 and 28 at. % Ni at 673 K, respectively. The maximum solid solubilities of Co in Ni$_{2-x}$Co$_x$In, Ni$_{13-x}$Co$_x$In$_9$, Ni$_{2-x}$Co$_x$In$_3$, and α-Ni$_{13-x}$Co$_x$ were about 3, 3.2, 8, and 60 at. % Co at 673 K.

3.2.2. Solid Solubility at 873 K

Figure 11a,b show the variation of the lattice parameter a and the lattice parameter c of Co$_{1-x}$Ni$_x$In$_2$ with the content of Ni, which indicated that the maximum solid solubility of Ni in Co$_{1-x}$Ni$_x$In$_2$ is $x = 0.612$ (about 20.19 at. % Co). The SEM micrograph of No. 26 is given in Figure 4b. The composition measurement of the light grey phase with composition of Co$_{20.10(5)}$Ni$_{16.82(5)}$In$_{63.08(6)}$, which was Co$_{1-x}$Ni$_x$In$_2$ ($x = 0.612$), suggested that the maximum solid solubility of Co in Co$_{1-x}$Ni$_x$In$_2$ was 20.1 at. % Co at 873 K. These two values are close. Although the binary CoIn$_2$ is absent at 873 K, the addition of Ni in CoIn$_2$ stabilized the compounds and kept the solid solution Co$_{1-x}$Ni$_x$In$_2$ with a wide range appeared at 873 K. The solid solubility range of Co$_{1-x}$Ni$_x$In$_2$ is 3-20.1 at. % Co at 873 K.

Figure 11. Variation of (a) the lattice parameter a and (b) lattice parameter c of Co$_{1-x}$Ni$_x$In$_2$ on Ni content.

The SEM micrograph of alloy No. 30 (Co$_{25}$Ni$_{45}$In$_{35}$) in Figure 12 clearly shows that the alloy contains three phases. Further composition measurements indicated that the grey phase with composition of Co$_{7.43(5)}$Ni$_{43.56(6)}$In$_{49.01(6)}$ was confirmed as Ni$_{1-x}$Co$_x$In ($x = 0.160$), the light grey phase with composition of Co$_{12.03(6)}$Ni$_{47.28(7)}$In$_{40.69(6)}$ was verified to be Ni$_{13-x}$Co$_x$In$_9$ ($x = 2.634$) and the dark phase with composition of Co$_{61.21(5)}$Ni$_{37.51(5)}$In$_{12.85(5)}$ was α-Ni$_{13-x}$Co$_x$ ($x = 0.600$). This further suggests that the maximum solid solubility of Co in Ni$_{13-x}$Co$_x$In$_9$ is about 12.03 at. % Co at 873 K.

Figure 12. The BSE micrograph of No. 30 (Co$_{25}$Ni$_{45}$In$_{35}$).
Similarly, the maximum solid solubilities of Co $\text{In}_{2-x}\text{Co}_x\text{In}$, $\text{Ni}_{13-x}\text{Co}_x\text{In}_2$, $\text{Ni}_{1-x}\text{Co}_x\text{In}$, $\text{Ni}_{2-x}\text{Co}_x\text{In}_3$, and $\alpha$-$\text{Ni}_{1-x}\text{Co}_x$ were found to be about 6, 12.03, 8, 9, and 60 at.% Co at 873 K, respectively. Both of the maximum solid solubilities of In in $\varepsilon$-$\text{Co}_{1-x}\text{Ni}_x$ and $\alpha$-$\text{Ni}_{1-x}\text{Co}_x$ were observed to be less than 3 at.% In.

Clearly, temperature has a great effect on the solid solubility of the third element in the binary compounds of the Co-Ni-In ternary system. Normally, the maximum solid solubilities of the third element increase with the increasing temperature. For example, the maximum solid solubilities of Co in $\text{Ni}_{13-x}\text{Co}_x\text{In}_6$ increased from 3.2 at.% Co at 673 K to 12.03 at.% Co at 873 K. However, the solid solubility range of $\text{Co}_{1-x}\text{Ni}_x\text{In}_2$ was found to be 0–18.64 at.% Ni at 673 K, while it shifted to the range of 3–20.1% at. % Ni at 873 K due to the absence of $\text{CoIn}_2$ at 873 K.

3.3. Isothermal Sections of the Co-Ni-In Ternary System at 673 K and 873 K

By comparing and analyzing more than 33 alloy samples of the Co-Ni-In ternary system and identifying the phases presented in each sample by XRD, optical microscopy, and SEM/EDS, the isothermal sections of the phase diagrams of the Co-Ni-In ternary system at 673 K and 873 K were determined. As shown in Figure 13, the isothermal section at 673 K consists of 11 single-phase regions, 21 two-phase regions, and 9 three-phase regions. The typical alloys and the details of the three-phase regions of the isothermal section of the Co-Ni-In ternary system are given in Table 2.

![Figure 13. Isothermal section of the Co-Ni-In system at 673 K.](image)

**Table 2. Typical samples and details of three-phase regions in the Co-Ni-In ternary system at 673 K.**

| Phase Regions | Samples | Alloy Compositions | Phase Components |
|---------------|---------|--------------------|------------------|
| 1             | No. 6   | Co0.5Ni0.5In22     | $\text{Ni}_{2-x}\text{Co}_x\text{In}$ (x = 0.09) + $\text{Ni}_2\text{In}$ + $\alpha$-$\text{Ni}_{1-x}\text{Co}_x$ (x = 0.40) |
| 2             | No. 7   | Co0Ni0.5In28       | $\text{Ni}_{13-x}\text{Co}_x\text{In}_6$ (x = 0.702) + $\text{Ni}_2\text{Co}_x\text{In}$ (x = 0.091) + $\alpha$-$\text{Ni}_{1-x}\text{Co}_x$ (x = 0.400) |
| 3             | No. 9   | Co0Ni0.45In35      | $\text{Ni}_{13-x}\text{Co}_x\text{In}_6$ (x = 0.702) + $\text{Ni}_{1-x}\text{Co}_x\text{In}$ (x = 0.125) + $\alpha$-$\text{Co}_{1-x}\text{Ni}_x$ (x = 0.600) |
| 4             | No. 10  | Co0Ni0.1In50       | $\text{Ni}_{13-x}\text{Co}_x\text{In}_6$ (x = 0.125) + Co$\text{Ni}_{1-x}\text{In}_x$ (x = 0.400) + $\varepsilon$-$\text{Co}_{1-x}\text{Ni}_x$ (x = 0.280) |
| 5             | No. 11  | Co0Ni0.2In40       | $\text{Ni}_{13-x}\text{Co}_x\text{In}_6$ (x = 0.565) + $\text{Ni}_{2-x}\text{Co}_x\text{In}_3$ (x = 0.400) + $\varepsilon$-$\text{Ni}_{1-x}\text{In}_x$ (x = 0.280) |
| 6             | No. 13  | Co0Ni0.1In30       | $\text{Ni}_{13-x}\text{Co}_x\text{In}_6$ (x = 0.125) + $\alpha$-$\text{Co}_{1-x}\text{Ni}_x$ (x = 0.600) + $\alpha$-$\text{Ni}_{1-x}\text{Co}_x$ (x = 0.280) |
| 7             | No. 14  | Co0Ni0.24In66      | $\text{Co}_{1-x}\text{Ni}_x\text{In}_2$ (x = 0.565) + $\text{Ni}_{2-x}\text{Co}_x\text{In}_3$ (x = 0.400) + $\text{Ni}_2\text{In}$ |
| 8             | No. 15  | Co6Ni0.12In72      | $\text{Co}_{1-x}\text{Ni}_x\text{In}_2$ (x = 0.565) + $\text{CoIn}_3$ + $\text{Ni}_3\text{In}$ |
| 9             | No. 16  | Co6Ni0.12In78      | $\text{CoIn}_3$ + $\text{Ni}_3\text{In}$ + In (Liquid) |

As shown in Figure 14, the isothermal section at 873 K contains 8 single-phase regions, 16 two-phase regions, and 8 three-phase regions. The typical alloys and the details of the three-phase regions of the Co-Ni-In isothermal section at 873 K are presented in Table 3.
By comparing the isothermal sections at 673 K and 873 K of phase diagram of the Co-Ni-In ternary system, the differences between the two sections can be found. The three three-phase regions, i.e., Co$_{1-x}$Ni$_x$In$_2$ (x = 0.565) + Ni$_{2-x}$Co$_x$In$_3$ (x = 0.4) + Ni$_3$In$_7$, Co$_{1-x}$Ni$_x$In$_2$ (x = 0.565) + CoIn$_3$ + Ni$_3$In$_7$ and CoIn$_3$ + Ni$_3$In$_7$ + In (Liquid) disappear due to the absence of the binary compounds Ni$_3$In$_7$ and CoIn$_3$ at 873 K [12,13], as seen Figure 4. The three-phase region Ni$_{13-x}$Co$_x$In$_9$ (x = 0.702) + Ni$_{1-x}$Co$_x$In$_2$ (x = 0.091) + α-Ni$_{1-x}$Co$_x$ (x = 0.400) breaks into two three-phase regions, i.e., Ni$_2$Co$_x$In$_3$ (x = 0.181) + α-Ni$_{1-x}$Co$_x$ (x = 0.500), and α + Ni$_3$In$_7$ + Ni$_3$Co$_x$In$_9$ (x = 2.634) + α-Ni$_{1-x}$Co$_x$ (x = 0.500) since the ε phase exist from 746 K to 1223 K [13]. According to the Co-Ni binary phase diagram, the crystal structures of Co$_{1-x}$Ni$_x$ alloys belong to the hexagonal structure when the concentration of Ni is less than 10 at. % Ni at 673 K, while its structure starts to change from a hexagonal structure into a cubic structure when Ni content exceed 10 at. % Ni. However, the Co$_{1-x}$Ni$_x$ alloy only crystallizes in a cubic structure at 873 K. Therefore, the three-phase region Ni$_{1-x}$Co$_x$In$_3$ (x = 0.125) + α-Co$_1$-xNi$_x$ (x = 0.600) + ε-Co$_{1-x}$Ni$_x$ (x = 0.280) at 673 K becomes a two-phase region, Ni$_{1-x}$Co$_x$In$_3$ (x = 0.160) + α-Ni$_{1-x}$Co$_x$ at 873 K. Although the binary compound CoIn$_3$ does not exist at 873 K, a narrow three-phase region, Co$_{1-x}$Ni$_x$In$_2$ (x = 0.091) + α-Co + In (Liquid), presents at 873 K due to the solid solution of Co$_{1-x}$Ni$_x$In$_2$ (x = 0.091–0.612) appearing at 873 K.
3.4. Crystal Structure

3.4.1. Crystal Structure of Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200)

The XRD and SEM/EDS data for the sample Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200) were collected in order to investigate its crystal structure. The XRD phase analysis points out that this sample is a single phase without any detectable impurity or additional phases. The SEM/EDS testing result shows that the composition of the sample is Ni34.62(3)Co5.23(4)In60.15(3), which reveals that 5.23(4)at.% of Co replaces the Ni position in Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200). To determine the crystal structures of the Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200) alloy, Rietveld refinement was performed from the XRD data by using the FullProf program. The powder X-ray diffraction pattern for the Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200) alloy is shown in Figure 15. The Rietveld refinement results of the alloys are listed in Table 4. The low values of the $R_p$ and $R_{wp}$ factors suggest that the fitted pattern is in good agreement with the experimental data and that the Rietveld refinement is reliable. The Rietveld refinement results support the case that the structure of sample remains unchanged at room temperature when cobalt is doped into the Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200) compound, and Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200) crystallizes in the Al$_2$Ni$_3$-type structure (space group P$\bar{5}$m1). The lattice parameters are $a = 0.43959(5)$ nm, $c = 0.53121(1)$ nm, and $Z = 1$. All positions are fully occupied in the compound. The Wyckoff 1a (0, 0, 0) site and 2d (1/3, 2/3, 0.3534 (3)) site are all occupied by In atoms, while the 2d (1/3, 2/3, 0.1381 (2)) site is occupied by Co and Ni atoms (0.1Co + 0.9 Ni).

![X-ray diffraction pattern](image_url)

*Figure 15. Observed, calculated, and differential XRD patterns of Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200).*
Table 4. Crystallographic data and Rietveld refinement results for Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200) and Co$_{1-x}$Ni$_x$In$_2$ (x = 0.54, 0.58) alloys.

| Compound                  | Phase                  | Structure Type | Space Group | Lattice Parameters (nm) | Atomic Parameters | Reliability Factors | Goodness of Fit |
|---------------------------|------------------------|----------------|-------------|-------------------------|-------------------|---------------------|-----------------|
| Ni$_{2-x}$Co$_x$In$_3$    | Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200) | Al$_2$Ni$_5$  | P6$_3$m1 (164) | a 0.43959(5) b 0.43959(5) c 0.53121(1) | In1 1a (0,0,0) 2d (1/3, 2/3, 1/6) + Co, Ni | Rp (%) 14.15 10.46 | S (%) 3.2 |
| Co$_{1-x}$Ni$_x$In$_2$   | Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540) | CuMg$_2$      | Fddd (70)    | a 0.9423(2) b 0.52823(3) c 1.7739(3) | In1 16e (0.9642, 1/4, 1/4) In2 16g (1/4, 1/4, 0.7123) | Rp (%) 12.58 10.29 | S (%) 2.7 |
| Co$_{1-x}$Ni$_x$In$_2$   | Co$_{1-x}$Ni$_x$In$_2$ (x = 0.580) | CuMg$_2$      | Fddd (70)    | a 0.9423(2) b 0.52823(3) c 1.7739(3) | In1 16e (0.9642, 1/4, 1/4) In2 16g (1/4, 1/4, 0.7123) | Rp (%) 12.58 10.29 | S (%) 2.7 |
| Ni$_{2-x}$Co$_x$In$_3$    | Ni$_{2-x}$Co$_x$In$_3$ (x = 0.400) | Al$_3$Ni$_5$  | P6$_3$m1 (164) | a 0.4397(1) b 0.4397(1) c 0.5319(3) | In2 2d (1/3, 2/3, 0.6412) | Rp (%) 12.58 9.89 | S (%) 2.7 |

M1 = 0.1Co + 0.9 Ni; M2 = 0.466Co + 0.534Ni; M3 = 0.438Co + 0.562Ni; M4 = 0.8Co + 0.2Ni
3.4.2. Crystal Structure of Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540, 0.580)

A large difference in the melting points of Co, Ni, and In (Co:1768K, Ni:1726K, In:429K) [37,38] causes difficulty in obtaining good single-phase Co$_{1-x}$Ni$_x$In$_2$ samples. Thus, the crystal structure of Co$_{1-x}$Ni$_x$In$_2$ was investigated with a few selected good single-phase samples. The crystal structure of Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540, 0.580) at 673 K was investigated via XRD and SEM/EDS. Figures 16 and 17 present the XRD patterns of Co$_{1-x}$Ni$_x$In$_2$. Table 4 lists the Rietveld refinement results of Co$_{1-x}$Ni$_x$In$_2$. The lower values of $R_p$ and $R_{wp}$ for the Rietveld refinement indicate that the refinement results are credible. The SEM/EDS results show that the composition of Co$_{1-x}$Ni$_x$In$_2$ (x = 0.580) is Co16.97(4)Ni18.02(3)In65.01(5); see Table S1. The refinement result shows that the Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540) compound, in which a large number of Co atoms are replaced by Ni, remains in the single phase and maintains the Cu$_2$Mg-type structure with the space group Fdd2 (No. 70). The lattice parameters of Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540) are refined to be $a = 0.9424(3)$ nm, $b = 0.5288(4)$ nm, and $c = 1.7742(5)$ nm. The Co$_{1-x}$Ni$_x$In$_2$ (x = 0.580) alloy contains the Co$_{1-x}$Ni$_x$In$_2$ (x = 0.565) (Cu$_2$Mg-type structure) phase with a small amount of the Ni$_2$Co$_{1-x}$In$_3$ (x = 0.400) (Al$_3$Ni$_2$-type structure). The EDS results show that the compositions of the Co$_{1-x}$Ni$_x$In$_2$ (x = 0.565) and Ni$_2$Co$_{1-x}$In$_3$ (x = 0.400) phases were about Co14.11(4)Ni18.64(3)In67.25(4) and Co7.41(3)Ni35.27(4)In57.3(4)2, which were identified as Co$_{1-x}$Ni$_x$In$_2$ (x = 0.565) and Ni$_2$Co$_{1-x}$In$_3$ (x = 0.400), respectively. This also proves that the solubility of Ni in Co$_{1-x}$Ni$_x$In$_2$ is 18.64 at.% Ni in the Ni$_2$Co$_{1-x}$In$_3$ (x = 0.400) alloy. The Rietveld refinement of the Co$_{1-x}$Ni$_x$In$_2$ (x = 0.580) alloy shows that the mass fractions of these two phases in the sample were 2.7% and 97.3%, respectively. The Rietveld refinement also indicated that the amount of Ni in the phase of Co$_{1-x}$Ni$_x$In$_2$ was $x = 0.565$. This is in agreement with the results of solid solubility determination including the SEM/EDS measurements. The refined lattice parameters of Co$_{1-x}$Ni$_x$In$_2$ (x = 0.565) are $a = 0.9421(2)$ nm, $b = 0.5282(3)$ nm, and $c = 1.7739(3)$ nm, which are slightly smaller than those of Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540). This phenomenon is mainly due to the similar crystal structure of Co and Ni, and the radius of Ni ($R_{Ni} = 0.124$ nm) atom is slightly smaller than that of Co ($R_{Co} = 0.125$ nm). The replacement of Ni atoms for Co atoms causes the volume of Co$_{1-x}$Ni$_x$In$_2$ to shrink. This results in smaller sizes. The lattice parameters of Ni$_2$Co$_{1-x}$In$_3$ (x = 0.400) are refined to be $a = 0.4397(1)$ nm and $0.5319(3)$ nm. In the structure of Co$_{1-x}$Ni$_x$In$_2$, the In atoms occupy the 16e and 16g sites, while Co atoms (including the substituting Ni atoms) exist at the 16g sites.

![Figure 16. Observed, calculated and differential XRD patterns of Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540).](image)
When the temperature increases from 482 to 528 K, the magnetization slowly drops to 1.05 emµ/g when temperature is heated from 430 K to 454 K under the 3 T magnetic field. The sample has weak (Equation (1)) by integrating the magnetization isotherms over the magnetic field.

\[ \Delta H_{\text{hys}} = (T_{\text{HS}} + T_{\text{HF}} - T_{\text{CS}} - T_{\text{CF}})/2 \]

This is very similar to the martensitic transformation phenomenon occurring in the Ni-Mn-A (A = Ga, Sn, In) \[39–41\] systems. As can be seen from the inset of Figure 18, the differential of magnetization to temperature varies with temperature and shows that the Curie temperature of the compound is 550 K.

3.5. Magnetic Properties

3.5.1. Magnetic Properties of Ni\(_{2-x}\)Co\(_x\)In\(_3\) (x = 0.200)

Figure 18 shows the zero-field-cooled (ZFC) and zero-field-heated (ZFH) temperature dependence of the magnetization under a static magnetic field of 50 mT for the Ni\(_{2-x}\)Co\(_x\)In\(_3\) (x = 0.200) alloy. During the heating process, the magnetization of the alloy remains constant at 0.044 emµ/g in the range of 5–436 K, and then increases sharply at 436 K (T\(_{\text{HS}}\)) and rises to 1.05 emµ/g at 451 K (T\(_{\text{HF}}\)). After that, the magnetization increases slowly and reaches a maximum of 1.11 emµ/g at 482 K. When the temperature increases from 482 to 528 K, the magnetization slowly drops to 1.05 emµ/g. The magnetization drops rapidly to a minimum value of 0.046 emµ/g with a further temperature increase to 560 K. The cooling curve almost completely coincides with the heating one, except in the temperature range of 339–451 K. In the cooling curve, the magnetization starts to decrease at 446 K (T\(_{\text{CS}}\)) and stops to decrease at 399 K (T\(_{\text{CF}}\)). The temperature cooling curve shifts to the low-temperature direction, indicating that the sample has thermal hysteresis in this temperature range; \(\Delta = 21\) K (\(\Delta T_{\text{hys}} = (T_{\text{HS}} + T_{\text{HF}} - T_{\text{CS}} - T_{\text{CF}})/2\)). This is very similar to the martensitic transformation phenomenon occurring in the Ni-Mn-A (A = Ga, Sn, In) \[39–41\] systems. As can be seen from the inset of Figure 18, the differential of magnetization to temperature varies with temperature and shows that the Curie temperature of the compound is 550 K.

Magnetization isotherms, measured during heating cycles at different temperatures, are shown in Figure 19. The samples show ferromagnetism at all measuring temperatures. Clearly, the magnetization increases with the increase in temperature. The magnetization increases from 0.178 emµ/g to 3.84 emµ/g when temperature is heated from 430 K to 454 K under the 3 T magnetic field. The sample has weak magnetism at 600 K—the magnetization is only 0.147 at 3 T. Magnetic entropy change (\(\Delta S_M\)) in the system, due to the application of external magnetic field, can be determined from Maxwell’s relation (Equation (1)) by integrating the magnetization isotherms over the magnetic field.

\[ \Delta S_M(T, H_{\text{max}}) = S_M(T, H_{\text{max}}) - S_M(T, 0) = \int_0^{H_{\text{max}}} \left( \frac{\partial M}{\partial H} \right) dH \]
Figure 18. The zero-field-cooled (ZFC) and zero-field-heated (ZFH) temperature dependence of the magnetization under static magnetic fields of 50 mT for the Ni$_{2-x}$Co$_x$In$_3$ ($x = 0.200$) alloy.

Figure 19. Magnetization isotherms of the Ni$_{2-x}$Co$_x$In$_3$ ($x = 0.200$) alloy.

Magnetic entropy changes in the alloy have been derived from the isothermal magnetization curves. Figure 20 shows the magnetic entropy change in the Ni$_{2-x}$Co$_x$In$_3$ ($x = 0.200$) sample as a function of temperature near 445 K under the 3 T, 2 T, and 1 T magnetic fields. Clearly, the greater the magnetic entropy, the stronger the magnetic field. The peak value under a field change of 3 T is 1.25 J kg$^{-1}$K$^{-1}$ at $T = 449.5$ K. The relative cooling power ($R_{CP} = \Delta S_M \times \Delta T_{FWHM}$), which is the measure of the amount of heat transfer between the cold and hot reservoirs in an ideal refrigeration cycle, is evaluated to be 14.125 J kg$^{-1}$K$^{-1}$ in the vicinity of 430–454 K for 3 T magnetic field change, where $\Delta T_{FWHM} = 11.3$ K.
with this magnetostructural transition, a large magnetic entropy change occurs. Figure 23 shows the XRD patterns, the main phase of the alloy at 490 K still was a Ni$_2$In$_3$ (x = 0.540) compound becomes larger. Under a magnetic field of 3 T, the magnetic entropy of the alloy (544 K and 553 K) can be obtained from the heating curve and the cooling curve. Representative isothermal magnetization loops measured around 462.5 K for Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540) are presented in Figure 22. The sample shows a low magnetization below 459 K, which rises from 0.21 emu/g to 4.46 emu/g with a temperature increase from 453 K to 471 K at the magnetic field of 3T. Associated with this magnetostructural transition, a large magnetic entropy change occurs. Figure 23 shows the magnetic entropy change as a function of temperature under the 3 T, 2 T, and 1 T magnetic fields for the alloy. It is clearly seen that as the magnetic field increases, the magnetic entropy of the Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540) compound becomes larger. Under a magnetic field of 3 T, the magnetic entropy of the alloy reaches a maximum of 1.475 J kg$^{-1}$K$^{-1}$ at about 463.5 K. The corresponding half-maximum width is $\Delta T_{FWHM} = 8.9$ K for the compound. The direct $R_C$ is evaluated as 13.128 J kg$^{-1}$K$^{-1}$.

Since the magnetization dependence of temperature (MT) curves of Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200) and Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540) are similar to those of ferromagnetic shape memory alloys with martensitic transformation, temperature-dependent powder XRD measurements were performed in order to obtain further insights into whether the compound undergoes martensite transformation behavior. Figure 24 shows the XRD patterns for the Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200) alloy measured at 490 K. According to XRD patterns, the main phase of the alloy at 490 K still was a Ni$_2$In$_3$ phase with an Al$_2$Ni$_3$-type structure. Furthermore, a small amount of Ni$_{10}$In$_{27}$ (space group Im-3 m) and Ni$_2$In (space group P63/mmc) appears in alloy. The results indicate that a small amount of Ni$_{10}$In$_{27}$ and Ni$_2$In is generated during heating. Indexing of the Ni$_2$In$_3$ phase showed that $a = 0.43905$ (5) nm, $c = 0.52930$ (3) nm, and $V = 0.08836$ nm$^3$. All these results show that a structure phase transformation but not a martensitic transformation occurred in Ni$_{2-x}$Co$_x$In$_3$ (x = 0.200) during heating. Figure 25 shows the XRD patterns of the Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540) alloy at 490 K, which still retains the Cu$_2$Mg-type structure type at 490 K. These results point to the notion that no martensitic transformation occurred in the Co$_{1-x}$Ni$_x$In$_2$ (x = 0.540) alloys during heating.
Figure 21. The ZFC and ZFH temperature dependence of the magnetization under static magnetic fields of 50 mT for the Co$_{1-x}$Ni$_3$In$_2$ ($x = 0.540$) compound.

Figure 22. Magnetization isotherms for the Co$_{1-x}$Ni$_3$In$_2$ ($x = 0.540$) alloy.

Figure 23. The magnetic entropy changes as a function of temperature under 3 T, 2 T, and 1 T magnetic fields for the Co$_{1-x}$Ni$_3$In$_2$ ($x = 0.540$) alloy.
There are eight Co-Ni-In binary compounds existing at 673 K and six binary compounds existing at 673 K and six binary compounds existing at 873 K. The solid solubility range of Co$_{2-x}$In$_2$ has been investigated. More than 130 samples were prepared and investigated by experimental methods to establish the phase equilibrium of the ternary Co-Ni-In system at 673 K and 873 K. The peculiar MT curves of Ni$_{2-x}$Co$_x$In$_3$ ($x = 0.200$) and Co$_{1-x}$Ni$_x$In$_2$ ($x = 0.540$) allow them to have potential to become magnetic functional materials.

1. There are eight Co-Ni-In binary compounds existing at 673 K and six binary compounds existing at 873 K. Compared to the phases at 673 K, the binary compounds Ni$_3$In$_7$, CoIn$_3$, and CoIn$_2$ disappeared, and ξ exists at 873 K.
2. The solid solubility range of Co$_{1-x}$Ni$_x$In$_2$ was found to be 0–18.64% at % Ni at 673 K, while it shifted to the range of 5–20.1% at % Ni at 873 K due to the absence of CoIn$_2$ at 873 K.
3. The isothermal section of the phase diagram of the Co-Ni-In system at 673 K consists of 11 single-phase regions, 21 two-phase regions, and 9 three-phase regions, and the isothermal section at 873 K contains 8 single-phase regions, 16 two-phase regions, and 8 three-phase regions.

4. Conclusions

More than 130 samples were prepared and investigated by experimental methods to establish the phase equilibrium of the ternary Co-Ni-In system at 673 K and 873 K. The peculiar MT curves of Ni$_{2-x}$Co$_x$In$_3$ ($x = 0.200$) and Co$_{1-x}$Ni$_x$In$_2$ ($x = 0.540$) allow them to have potential to become magnetic functional materials.
Three-phase regions disappear due to the absence of the binary compounds Ni₃In₇ and CoIn₃ at 873 K. The three-phase region Ni₁₃₋ₓCoₓIn₉ (x = 0.702) + Ni₁₋ₓCoₓIn₂ (x = 0.091) + α-Ni₁₋ₓCoₓ (x = 0.400) breaks into two three-phase regions due to the ε phase existing at 873 K.

4. The MT curves of Ni₂₋ₓCoₓIn₃ (x = 0.200) and Co₁₋ₓNiₓIn₂ (x = 0.540), which are similar to the Ni-Mn-A (A = Ga, Sn, In), do not undergo martensitic transformation at temperatures, which results in a sharp change in magnetization. The maximum magnetic entropy changes of Ni₂₋ₓCoₓIn₃ (x = 0.200) and Co₁₋ₓNiₓIn₂ (x = 0.540) under 3T in 430 K–454 K and 454 K–472 K are 1.25 J kg⁻¹K⁻¹, 1.475 J kg⁻¹K⁻¹, respectively.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/1996-1944/13/18/3990/s1, Table S1: XRD and SEM/EDS analysis results of the selected Co-Ni-In samples at 673 K, Table S2: XRD and SEM/EDS analysis results of the selected Co-Ni-In samples at 873 K.

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