JOURNAL OF SOLID STATE CHEMISTRY 43, 354–358 (1982)

The Ferromagnetic and Paramagnetic Properties of Heusler Alloys $(Ni_{1-x}Co_x)_2MnSn$

E. UHL

Institut für Physikalische Chemie, Universität Wien,
A-1090 Währingerstrasse 42, Austria

Received December 28, 1981; in final form March 29, 1982

Mixed Heusler alloys with composition $(Ni_{1-x}Co_x)_2MnSn$ (x = 0–1) were prepared. They were single phase with $L2_1$ structure. Magnetic measurements were undertaken in the ferromagnetic and paramagnetic regions. Magnetic parameters, such as Curie temperature, paramagnetic Curie temperature, and spontaneous moment μ_{00} depend linearly on the composition. The linear variation of μ_{00} is phenomenologically interpreted by a linear variation of the magnetic moment of manganese between 4.0 μ_B for Ni_2MnSn to 3.6 μ_B for Co_2MnSn, cobalt having a constant moment of 0.75 μ_B over the whole concentration range.

1. Introduction

Heusler alloys are magnetically ordered ternary intermetallic compounds of composition X_2YZ with the cubic $L2_1$ structure (Fig. 1). Chemical flexibility of the system allows substitution of X, Y, and Z in a wide range of composition. Therefore the influence of different ions on the three possible sites in the lattice can be studied.

The first representatives were alloys where Y was manganese and X a nonferromagnetic metal (*1*). Now about 30 Heusler alloys are known with Y = Mn. X atoms are Fe, Co, Rh, Ir, Ni, Pd, Pt, Cu, and Au (see Table I). It is known from many investigations that Mn carries a localized moment of approx 4 μ_B. Contrary to Ni, which has no moment, Co displays a moment of approx 0.7 μ_B. With the help of neutron diffraction measurements Webster (*2*) found 3.6 μ_B for Mn and 0.75 μ_B for Co in Co–Mn Heusler alloys.

One aspect of this work was to study the change in magnitude of the moments substituting Ni by Co. The relationship of Co and Ni suggests the investigation of Heusler alloys with composition $(Ni_{1-x}Co_x)_2MnSn$.

2. Experimental

2.1. Alloy preparation. Alloys of the system $(Ni_{1-x}Co_x)_2MnSn$, with x = 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.95, 1.0, were prepared. Appropriate amounts of ≥ 99.9% pure Ni, Co, Mn, and Sn powders were thoroughly mixed, pressed to pills, and sintered in evacuated quartz ampoules. Tin, the component with the lowest melting point, was brought to reaction with the other metals by heating the samples to 200°C (for 6 hr), 230°C (for 12 hr), and 300°C (12 hr). With this treatment the reaction of the tin with the other constituents was ensured. Then the samples were sintered for 3 days at 800°C. The alloys were quenched in ice water and the quartz capsules were broken under water immediately. The resulting ingots were powdered, pressed to pills, and annealed at 800°C for 3

0022-4596/82/090354-05$02.00/0

TABLE I

PREFERRED SITES OF DIFFERENT ATOMS IN KNOWN HEUSLER ALLOYS X_2YZ (X, Y ARE TRANSITION METALS AND Z IS FROM THE GROUP OF *sp* ELEMENTS)

	Y sites					*X* sites			*Z* sites			
	IIIB	IVB	VB	VIB	VIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA
1												
2									B	C	N	O
3									Al	Si	P	S
4	Sc	Ti	V	Cr	Mn	Fe Co Ni	Cu	Zn	Ga	Ge	As	Se
5	Y	Zr	Nb	Mo	Tc	Ru Rh Pd	Ag	Cd	In	Sn	Sb	Te
6	La	Hf	Ta	W	Re	Os Ir Pt	Au	Hg	Tl	Pb	Bi	Po

days again. After quenching as above the ingots were powdered partially and checked by X-ray powder methods.

2.2. Structural analysis. Specimens were identified and characterized by Debye–Scherrer powder photographs, using vanadium-filtered Cr*Kα* radiation. All samples were single phased with the highly ordered $L2_1$ structure.

2.3. Magnetic measurements. Magnetic measurements were performed on a Faraday pendulum magnetometer[1] in the temperature range between 80 and 1200K and at applied fields up to 12.3 kOe in a 40-mbar high-purity helium/argon atmosphere. Magnetization measurements were calibrated with Ni (*3*), and susceptibility measurements with $CuSO_4 \cdot 5H_2O$ ($\chi_g^{293} = 6.00 \times 10^{-6}$ emu g^{-1}).

Spontaneous magnetization σ_{0T} was obtained by an extrapolation of the magnetization at different fields, σ_{HT}, against H. σ_{00}, the spontaneous magnetization at $T = 0$, was obtained by using a $T^{3/2}$ law. To make sure that only one ferromagnetic phase was present, the smoothness of the magnetization curves was given special attention. The Curie points, θ_F, were obtained by using a modified Arrott plot (σ^2 against H/σ; (*4*)). To eliminate the influence of other ferromagnetic phases in the paramagnetic region, a Honda–Owen plot (*5*) was used. The applied fields were 7.39–12.30 kOe.

3. Results

3.1. Co_2MnSn. Our results of the Heusler alloy Co_2MnSn are compiled in comparison with literature data in Table II. θ_P was determined for the first time. There is very good agreement with the data of Webster (*2, 6*).

3.2. Ni_2MnSn. Results for Ni_2MnSn can be seen in Table III. They are in very good correspondence to recently published data.

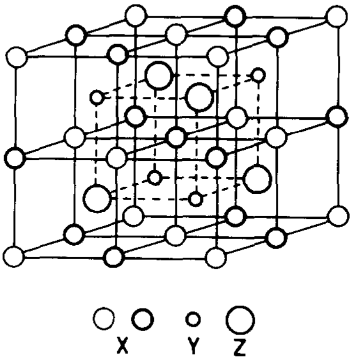

FIG. 1. The X_2YZ Heusler structure ($L2_1$, *Fm3m*).

---

[1] SUS 10, A. Paar KG, Graz, Austria.

TABLE II

LATTICE PARAMETER a (Å), CURIE TEMPERATURE θ_F (K), PARAMAGNETIC CURIE TEMPERATURE θ_P (K), FERROMAGNETIC MOMENT μ_{00} (μ_B), AND PARAMAGNETIC MOMENT μ_{eff} (μ_B) OF THE COMPOUND Co_2MnSn

a (Å)	θ_F (K)	θ_P (K)	μ_{00} (μ_B)	μ_{eff} (μ_B)	Data from
5.989	830	—	—	—	(*7*, *8*)
6.003	—	—	—	—	(*9*)
5.977	811	—	4.79	—	(*10*)
6.000	829	—	5.08	—	(*2*, *6*)
5.995	857	—	4.8	—	(*11*)
6.01	770	—	5.26	4.6	(*12*)
5.999	825	856	5.02	5.29	This work

3.3. *($Ni_{1-x}Co_x)_2MnSn$.* Experimental data of this investigation are summarized in Tables IV and V, and are displayed in Figs. 2 and 3. Magnetic parameters, such as θ_F, θ_P, and μ_{00}, seem to vary linearly with the composition.

4. Discussion

TABLE III

LATTICE PARAMETER a (Å), CURIE TEMPERATURE θ_F (K), PARAMAGNETIC CURIE TEMPERATURE θ_P (K), FERROMAGNETIC MOMENT μ_{00} (μ_B), AND PARAMAGNETIC MOMENT μ_{eff} (μ_B) OF THE COMPOUND Ni_2MnSn

a (Å)	θ_F (K)	θ_P (K)	μ_{00} (μ_B)	μ_{eff} (μ_B)	Data from
6.048	410	—	—	—	(*7*, *8*)
6.057	—	—	—	—	(*9*)
6.052	344	—	4.05	—	(*6*)
6.032	342	—	3.69	—	(*10*)
6.034	—	—	—	—	(*13*)
6.050	358	—	3.8	—	(*11*)
6.062	345	359	4.04	5.05	(*14*)
6.053	345	—	4.07	—	(*15*)
6.05	340	—	3.25	4.55	(*16*)
6.052	342	363	3.98	4.90	This work

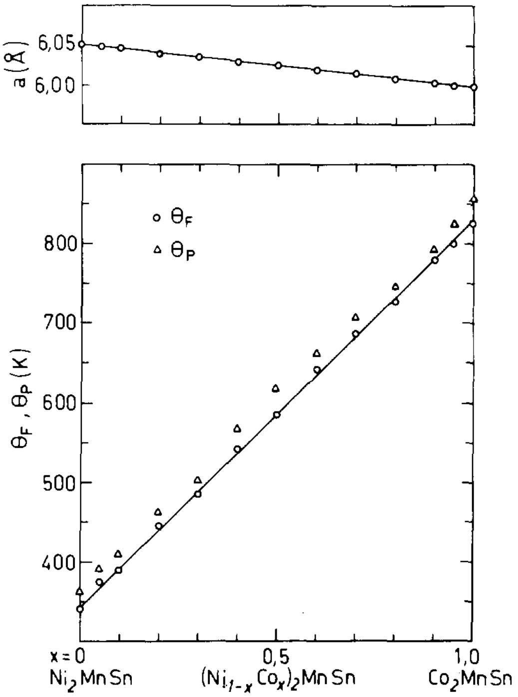

FIG. 2. Lattice parameter a (Å), Curie temperature θ_F (K), and paramagnetic Curie temperature θ_P (K) of $(Ni_{1-x}Co_x)_2MnSn$. Straight lines connect the values of the ternary alloys.

It is known from many investigations that Mn carries a moment of approx 4 μ_B in Heusler alloys. In Heusler alloys with Co, however, a magnetic moment of only 3.6–3.0 μ_B has been determined by neutron diffraction (*2*). The value of the moment for Co is 0.75 μ_B.

One reason for this investigation was the interest in the variation of the Mn moment from Ni_2MnSn (4 μ_B) to Co_2MnSn (3.6 μ_B). The experimental magnetic moment per formula unit $\mu_{00_{exp}}$ of $(Ni_{1-x}Co_x)_2MnSn$ alloys can be very well reproduced assuming a linear variation of the manganese moment with the x parameter between the values of the ternaries ($\mu_{00_{Mn}} = 4.0$ for Ni_2MnSn and 3.6 for Co_2MnSn), the moment of Co staying constant ($\mu_{00_{Co}} = 0.75$) (Table IV).

We tried to explain the variation of the Mn moment assuming little chemical disorder increasing with the Co concentration. A small amount of chemical disorder is indicated for Co_2MnSn in a recent paper (*17*).

TABLE IV

SPONTANEOUS MAGNETIZATION $\sigma_{00_{exp}}$ (emu g^{-1}), FERROMAGNETIC SATURATION MOMENT $\mu_{00_{exp}}$ (μ_B), AND CURIE TEMPERATURE θ_F (K) OF $(Ni_{1-x}Co_x)_2MnSn$

Alloy	$\sigma_{00_{exp}}$ (emu g^{-1})	$\sigma_{00_{calc}}$ (emu g^{-1})	$\mu_{00_{exp}}$ (μ_B)	$\mu_{00_{calc}}$ (μ_B)	$\theta_{F\ exp}$ (K)	$\theta_{F\ calc}$ (K)
Ni_2MnSn	76.3	76.7	3.98	4.00	342	344
$Ni_{1.9}CO_{0.1}MnSn$	76.7	77.8	4.00	4.06	375	368
$Ni_{1.8}Co_{0.2}MnSn$	81.2	78.8	4.23	4.11	390	393
$Ni_{1.6}Co_{0.4}MnSn$	82.0	80.9	4.28	4.22	446	441
$Ni_{1.4}Co_{0.6}MnSn$	85.0	83.0	4.43	4.33	486	490
$Ni_{1.2}Co_{0.8}MnSn$	86.5	85.1	4.51	4.44	543	538
$Ni_{1.0}Co_{1.0}MnSn$	87.2	87.2	4.55	4.55	585	587
$Ni_{0.8}Co_{1.2}MnSn$	91.0	89.3	4.75	4.66	642	635
$Ni_{0.6}Co_{1.4}MnSn$	92.3	91.4	4.82	4.77	687	684
$Ni_{0.4}Co_{1.6}MnSn$	93.8	93.5	4.89	4.88	728	732
$Ni_{0.2}Co_{1.8}MnSn$	94.3	95.6	4.92	4.99	779	781
$Ni_{0.1}Co_{1.9}MnSn$	97.0	96.7	5.04	5.05	800	805
Co_2MnSn	96.2	97.7	5.02	5.10	825	829

Note. The calculated values $\mu_{00_{calc}}$, $\sigma_{00_{calc}}$, are explained in the text. $\theta_{F\ calc}$ is obtained by linear interpolation between the values of the ternaries.

From $Ni_2Mn(Mn_xSn_{1-x})$ (*18*) it is known that Mn on Z sites (Fig. 1) orders antiferromagnetically to Mn on Y sites because of the smaller Mn–Mn distances. This effect is also known from diluted PdMn (*19*), AgMn (*20*), and CuMn (*21*) alloys. Independently other authors (*22*) drew the conclusion of an antiferromagnetic ordering of Mn on Z sites with respect to the Mn sublattice. There are even smaller distances for Mn atoms on X sites. Five percent of antiferromagnetically ordered Mn atoms on sites other than on the Y sublattice (Fig. 1) would reduce the net moment for Mn from 4 to 3.6 μ_B. Intensity calculations of neutron diffraction patterns and comparison with Webster's experimental data (*2*), however, are not in favor of such an interpretation. Especially, antiferromagnetically ordered Mn on Z sites would significantly influence both nuclear and magnetic reflections with *hkl* all odd, e.g., (111) and (311). Therefore the reduced magnetic moment of Mn is probably due to Co–Mn interactions. A similar increase of the magnetic moment of Mn with decreasing Co concentration has been observed in the system $(Cu_{1-x}Co_x)_2MnSn$ (*23*).

TABLE V

PARAMAGNETIC MOMENT $\mu_{eff\ exp}$ (μ_B), PARAMAGNETIC CURIE TEMPERATURE θ_P (K), AND LATTICE PARAMETER a_{exp} (Å) OF $(Ni_{1-x}Co_x)_2MnSn$

Alloy	$\mu_{eff\ exp}$ (μ_B)	θ_P (K)	a_{exp} (Å)	a_{calc} (Å)
Ni_2MnSn	4.90	363	6.052	6.052
$Ni_{1.9}Co_{0.1}MnSn$	4.85	392	6.049	6.050
$Ni_{1.8}Co_{0.2}MnSn$	4.87	410	6.047	6.047
$Ni_{1.6}Co_{0.4}MnSn$	5.07	463	6.041	6.040
$Ni_{1.4}Co_{0.6}MnSn$	5.05	503	6.036	6.037
$Ni_{1.2}Co_{0.8}MnSn$	4.99	568	6.031	6.032
$Ni_{1.0}Co_{1.0}MnSn$	5.03	617	6.026	6.025
$Ni_{0.8}Co_{1.2}MnSn$	5.14	664	6.020	6.022
$Ni_{0.6}Co_{1.4}MnSn$	5.10	708	6.015	6.016
$Ni_{0.4}Co_{1.6}MnSn$	5.19	748	6.010	6.010
$Ni_{0.2}Co_{1.8}MnSn$	5.23	785	6.004	6.006
$Ni_{0.1}Co_{1.9}MnSn$	5.26	825	6.002	6.001
Co_2MnSn	5.29	856	5.999	5.999

Note. a_{calc} is obtained by linear interpolation between the a values of the ternaries.

Whereas, from Ni_2 MnSn to Co_2 MnSn only, there is a small decrease of the lattice parameters ($\Delta a < 1\%$) there is a considerable

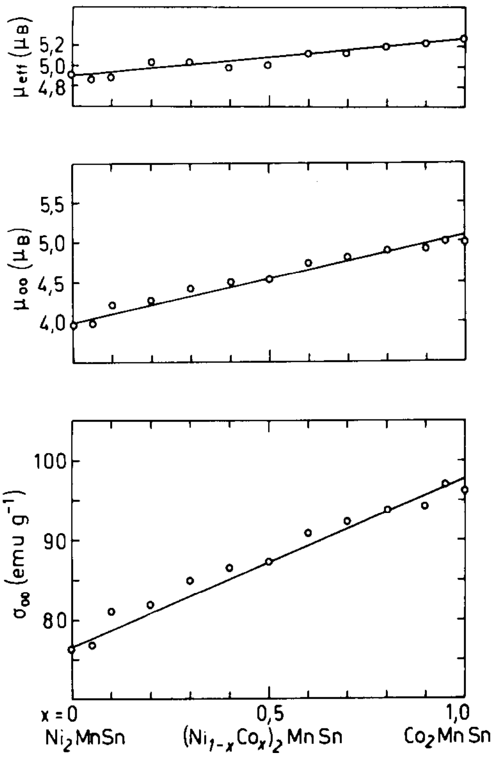

FIG. 3. Paramagnetic moment μ_{eff} (μ_B), ferromagnetic moment μ_{00} (μ_B), and magnetization σ_{00} (emu g^{-1}) of $(Ni_{1-x}Co_x)_2MnSn$. Straight lines represent the calculated values.

increase in Curie temperatures. Therefore from Ni_2MnSn to Co_2MnSn the increase of θ_F is due to the increase of Co–Mn and Co–Co interactions (Fig. 2). The linear variation of θ_F and θ_P in the alloy $(Ni_{1-x}Co_x)_2MnSn$ is in contrast to that of the $(Cu_{1-x}Co_x)_2MnSn$ (*23*) and $(Ni_{1-x}Cu_x)_2MnSn$ (*24*) systems, which exhibit minima in these parameters. These minima have been interpreted as the result of the interplay of the Co–Co and Co–Mn interactions in the first case. The minimum in the second system has been explained as a superposition of increasing d_t–d_1 interactions (*25*) and lattice enlargement.

Acknowledgment

The author gratefully acknowledges the financial support of the "Fonds zur Förderung der wissenschaftlichen Forschung in Österreich" (Project 4013).

References

1. F. HEUSLER., *Verh. Dtsch. Phys. Ges.* **5,** 219 (1903).
2. P. J. WEBSTER., *J. Phys. Chem. Solids* **32,** 1221 (1971).
3. J. CRANGLE AND G. M. GOODMAN, *Proc. Roy. Soc. London Ser. A* **321,** 477 (1971).
4. J. S. KOUVEL, General Electric Research Report 57-RL-1799 (1957).
5. K. HONDA AND M. OWEN, *Ann. Phys. (Leipzig)* **32,** 1048 (1910); and **37,** 657 (1912).
6. P. J. WEBSTER, *Contemp. Phys.* **10,** 559 (1969).
7. L. CASTELLIZ, *Monatsh. Chem.* **84,** 765 (1953).
8. L. CASTELLIZ, *Z. Metallkd.* **46,** 198 (1955).
9. P. I. KRIPYAKEVICH, E. I. GLADYSHEVSKII, AND O. S. ZARECHNYNK, *Dokl. Akad. Nauk SSSR* **95,** 525 (1954).
10. T. SHINOHARA, *J. Phys. Soc. Japan* **28,** 313 (1970).
11. A. SZYTULA, A. KOLODZIEJCZYK, H. RZANY, J. TODOROVIC, AND A. WANIC, *Phys. Status Solidi A* **11,** 57 (1972).
12. R. SOBCZAK, *Monatsh. Chem.* **107,** 977 (1976).
13. W. LEIPER, D. J. W. GELDART, AND P. J. POTHIER, *Phys. Rev. B* **3,** 1637 (1971).
14. C. C. M. CAMPBELL AND C. V. STAGER, *Canad. J. Phys.* **54,** 2197 (1976).
15. R. A. MACDONALD AND C. V. STAGER, *Canad. J. Phys.* **55,** 1481 (1977).
16. R. SOBCZAK, *Monatsh. Chem.* **109,** 455 (1978).
17. R. A. DUNLAP, R. H. MARCH, AND G. STROINK, *Canad. J. Phys.* **59,** 1577 (1981).
18. C. V. STAGER AND C. C. M. CAMPBELL, *Canad. J. Phys.* **56,** 674 (1978).
19. W. M. STAR, S. FONER, AND E. J. MCNIFF, *Phys. Rev.* **12,** 2690 (1975).
20. L. NÉEL, *Proc. Phys. Soc. (London) A* **395,** 870 (1952).
21. J. S. KOUVEL, *J. Phys. Chem. Solids* **24,** 795 (1963).
22. LE DANG KHOI, P. VEILLET, AND I. A. CAMPBELL, *J. Phys. F* **7,** L237 (1977).
23. E. UHL, *J. Magn. Magn. Mater.* **25,** 221 (1981).
24. E. UHL, *Monatsh. Chem.* **113,** 275 (1982).
25. M. B. STEARNS, *J. Magn. Magn. Mater.* **15–18,** 301 (1980).