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EFFECT OF HYDROSTATIC PRESSURE ON THE CURIE TEMPERATURE OF THE HEUSLER ALLOYS Ni_2MnZ(Z = Al, Ga, In, Sn AND Sb)

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The pressure derivative of the Curie temperature dT_c/dp of the Heusler alloys Ni_2MnZ(Z = Al, Ga, In, Sn and Sb) has been obtained from the results of temperature dependence of initial permeability under pressure up to about 6 kbar. For all alloys the Curie temperatures increase linearly with increasing pressure at the rate of dT_c/dp: +0.7 K/kbar for Ni_2MnAl, +1.0 K/kbar for Ni_2MnGa, +0.9 K/kbar for Ni_2MnIn, +1.4 K/kbar for Ni_2MnSn and +4.0 K/kbar for Ni_2MnSb. On the basis of these results, the interatomic dependence of the exchange interaction for Heusler alloys is discussed. The magnetic susceptibilities of those alloys are also reported.

1. Introduction

The effect of pressure on the Curie temperature has been studied in a number of ferromagnets to obtain information on the volume dependence of the exchange interaction. Especially, an occurrence of ferromagnetism in manganese alloys and compound has been discussed in terms of the dependence of exchange interaction on the interatomic distance between manganese ions. Guillaud [1] discussed the existence of a critical value for the distance between Mn atoms for the ferromagnetism. Castelliz [2] proposed an empirical curve, in which the Curie temperature of ferromagnetic alloys and compounds containing manganese ions are plotted against the ratio of nearest interatomic distance between magnetic ions to the radius of magnetic ion. From the Castelliz's curve, the compounds MnSb, MnAs and MnBi are expected to have a negative pressure coefficient of the Curie temperature. On the other hand, the Heusler alloys Ni_2MnSn, Ni_2MnSb, Cu_2MnIn and the cubic Cl_b-type compounds $Pt_{1-x}Au_x$ MnSb($0 \leqslant x \leqslant 1$) are expected to have a positive pressure coefficient of the Curie temperature. In fact, the pressure coefficient of the Curie temperature obtained for these compounds is consistent with that expected from the Castelliz's curve [3–9]. However, it is not clear at present whether the Castelliz's curve is adaptable for all manganese compounds. So, it is necessary to examine systematically the pressure effect on the Curie temperature of many manganese compounds and alloys beside the compounds mentioned above.

Ferromagnetic Heusler alloys Ni_2MnZ(Z = Al, Ga, In, Sn and Sb) have the $L2_1$-type crystal structure (fig. 1). The Ni atoms occupy the corner (a, c) sites of the bcc structure, while the Mn and

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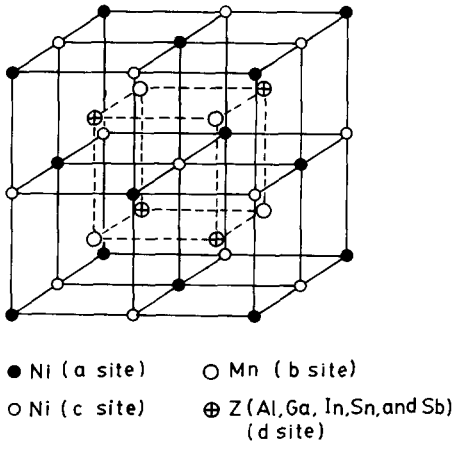

Fig. 1. The Heusler structure.

Z atoms occupy alternate body center (b and d, respectively) sites. The crystal structure of the Cl_b-type compounds is analogous to that of the $L2_1$-type compounds except that the atoms on the site c in the $L2_1$-type compounds are lacking in the Cl_b-type compounds. Various magnetic studies [10–12] and unpolarized neutron diffraction studies [13,14] for Ni_2MnZ have suggested that the magnetic moments of about $4\mu_B$ are confined only to the Mn atoms. The nearest interatomic distance between maganese atoms in these alloys ranges from 4.3 to 4.1 Å. So, it is expected from the Castelliz's curve that the pressure derivative of the Curie temperature in these alloys are all positive. The main purpose of the present paper is to measure the pressure change of the Curie temperature of ferromagnetic alloys Ni_2MnZ under hydrostatic pressure and to investigate the interatomic distance dependence of the exchange interaction of these compounds.

2. Experimental details

Polycrystalline samples of Ni_2MnZ (Z = Al, Ga, In, Sn and Sb) were prepared from Ni (99.9%), Mn (99.99%), Al (99.9999%), Ga (99.9%), In (99.9999%), Sn (99.9999%) and Sb (99.9%). They were mixed in the desired proportion, sealed in evacuated silica tubes and melted at about 1200°C. They were then annealed for 24 h at about 900°C and quenched. The reaction products were pulverized, mixed, heated again in vacuum at 900°C for 96 h and then quenched.

X-ray powder diffraction patterns which obtained at room temperature using copper radiation indicated a single phase, ordered $L2_1$-type structure. For Ni_2MnAl and Ni_2MnGa, the similarity of X-ray scattering amplitudes of the component elements precluded quantitative determination of the chemical order. For Ni_2MnAl, Ziebeck and Webster [13] reported that (a) a quenched alloy: half the Mn and Al atoms interchanged sites randomly and the structure reduced to the simply ordered B2, CsCl-type, (b) a slowly cooled alloy: there were some regions of $L2_1$-type order. The lattice parameter of samples in this system are shown in table 1. These results are consistent with those previously observed by Webster [10].

The thermal variation of the static susceptibility was determined using a sensitive magnetic balance at temperatures from 300 to 780 K.

Hydrostatic pressure was applied to a sample in a Teflon pressure sample cell filled with a silicon oil by using a piston-cylinder type device [8]. In this Teflon cell, a sample was placed in a cylindrical cell made of BN with high thermal conductivity. The temperature was measured with a chromel–alumel thermocouple, kept in contact with the sample. The shape of samples for high pressure measurements was a rod. Those were prepared by forcing powder sample into a silica tube about 1 mm in diameter, and annealing it at 900°C under vacuum. The Curie temperature was determined by an ac transformer method. The primary and secondary coils were wound on the

Table 1
A summary of the magnetic properties of the Ni_2MnZ(Z = Al, Ga, In, Sn and Sb)

Compound	a (Å)	T_c (K)	θ_p (K)	p_{eff} (μ_B)	μ/Mn (μ_B)
Ni_2MnAl	5.824	317	160	4.90	4.0
Ni_2MnGa	5.805	355	374	4.59	3.7
Ni_2MnIn	6.070	315	350	4.69	3.8
Ni_2MnSn	6.048	328	355	5.00	4.1
Ni_2MnSb	6.027	331	400	4.20	3.3

sample rods. An ac current of a constant amplitude flowed in the primary coil and the second voltage, which is directly proportional to initial permeability, was recorded as a function of temperature at various pressures. The pressure was calibrated by using the Hg solid–liquid transition temperature.

3. Experimental results

3.1. Susceptibility

For the prepared alloys, the temperature dependence of the inverse susceptibility $1/\chi$ above the Curie temperature was studied in the temperature range from 300 to 780 K. The results of Ni_2MnZ(Z = Ga, In and Sn) are shown in fig. 2. The observed $1/\chi$ vs. temperature curves can be well expressed by the Curie–Weiss law. From these results, the paramagnetic Curie temperature Θ_p and the effective Bohr magneton p_{eff} were determined, the results of which are tabulated in table 1. The value of p_{eff} for each alloys determined in the present experiment agreed fairly well with those reported by Webster [10]. Assuming that the orbital moment is in a quenched state, magnetic moments were calculated from the p_{eff} in table 1. They are about $4\mu_B$ per molecule. In the case of Ni_2MnSb, the inverse susceptibility

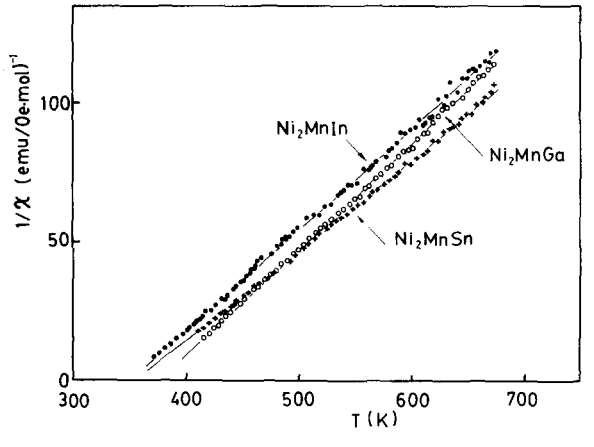

Fig. 2. Inverse susceptibility vs. temperature curves for Ni_2MnZ(Z = Ga, In and Sn).

Table 2
Pressure coefficient of the Curie temperature for Ni_2MnZ

Compound	$(1/T_c)(dT_c/dp)$ (kbar^{-1})
Ni_2MnAl	$+2.27\times10^{-3}$
Ni_2MnGa	$+2.82\times10^{-3}$
Ni_2MnIn	$+2.86\times10^{-3}$
Ni_2MnSn	$+4.27\times10^{-3}$
Ni_2MnSb	$+12.0\times10^{-3}$

$1/\chi$ vs. temperature curve follows the Curie–Weiss law in temperatures above 610 K with the paramagnetic Curie temperature 400 K. However, below 610 K the inverse susceptibility $1/\chi$ deviates downward from the extension of the linear part of the curve. The origin of the deviation is not clear at present. The inverse susceptibility of Ni_2MnAl also follows the Curie–Weiss law with the paramagnetic Curie temperature 160 K. Though it is reported that both the quenched and slow-cooled alloys, Ni_2MnAl, with B2 order have an antiferromagnetic cone spiral structure [13], ferromagnetism was observed in this experiment as described in section 3.2. The paramagnetic Curie temperature is usually higher than the Curie temperature in the ferromagnets. However, in the case of Ni_2MnAl the paramagnetic Curie temperature is lower than the Curie temperature. The occurrence of ferromagnetism for Ni_2MnAl may be attributed to the presence of small dispersed regions of $L2_1$ order which might be expected to be ferromagnetic [13].

3.2. Pressure effect on the Curie temperature

Fig. 3 shows initial permeability vs. temperature curves for Ni_2MnIn at different pressures. As seen in the figure, initial permeability decreases rapidly just below the Curie temperature with increasing temperature and then takes a nearly constant value with further rise in temperature. The Curie temperature was defined as the point of intersection of linear extrapolations from both the higher and lower temperature ranges as shown in the figure. The Curie temperature was found to shift from 315.0 K at normal pressure to 319.6 K under a pressure of 5.2 kbar. Similar curves at

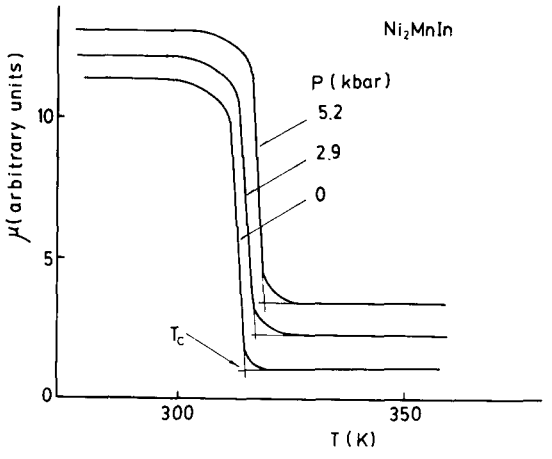

Fig. 3. Permeability vs. temperature curves under hydrostatic pressures for Ni_2MnIn.

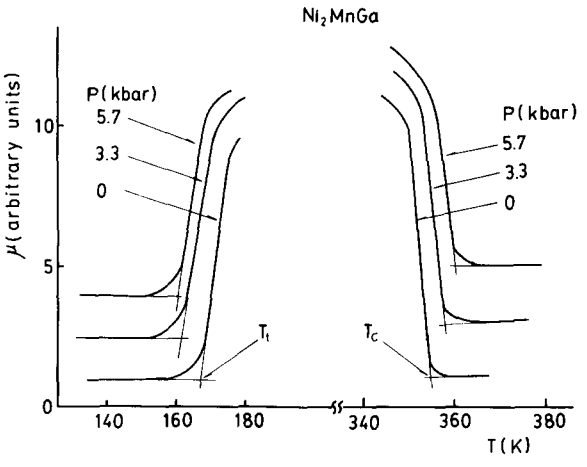

Fig. 5. Permeability vs. temperature curves under hydrostatic pressures for Ni_2MnGa.

various pressures were also obtained for Ni_2MnZ with Z = Al, Ga, Sn and Sb. The pressure shifts of the Curie temperature ΔT_c for Ni_2MnIn are shown against applied pressure in fig. 4.

Fig. 5 shows initial permeability vs. temperature curves for Ni_2MnGa at different pressures. These magnetic features in the high temperature range are similar to that of Ni_2MnIn. However, there was an abrupt change of the permeability in the low temperature range, as shown in fig. 5. Below 169 K (at normal pressure) the specimen becomes much more hard to magnetize. According to the results of a neutron diffraction for Ni_2MnGa [14], a martensitic phase transition to a

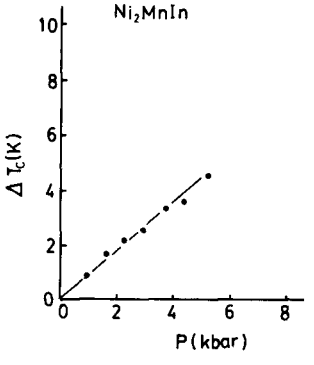

Fig. 4. The shift of the Curie temperature vs. pressure curve for Ni_2MnIn.

complex tetragonal structure occurs on cooling. So, the occurrence of magnetic hardening at low temperature may be due to an increase of the magnetic anisotropy and a reduction in the number of easy axes of magnetization aligned in a direction close to the direction of the applied field. The pressure dependence of the Curie temperature T_c and the structural phase transition temperature T_t are shown in fig. 6. It is found that T_t decreases linearly with increasing applied pressure. The value of dT_c/dp is -1.5 deg/kbar. As shown in fig. 4 and 6, the Curie temperatures of Ni_2MnIn and Ni_2MnGa were found to increase linearly with applied pressure in the pressure range investigated. The values of $(1/T_c)\,(dT_c/dp)$ determined from the present experimental results are shown in table 2. In Ni_2MnAl, Ni_2MnSn and Ni_2MnSb, the permeability vs. temperature curves show changes in slope at T_c similar to that in fig. 3. For Ni_2MnIn, the value of $(1/T_c)\,(dT_c/dp)$ is comparable with the value given by Austin and Mishra [7]. For Ni_2MnSn, the value of $(1/T_c)\,(dT_c/dp)$ is large compared with the values given by Austin and Mishra [7], and Kaneko et al. [8]. For Ni_2MnSb, the value is somewhat larger than the value reported by Kaneko et al. [8]. However, Austin and Mishra [7] reported that the pressure derivative of the Curie temperature for Ni_2MnSb is nearly zero. It should be noted that the values

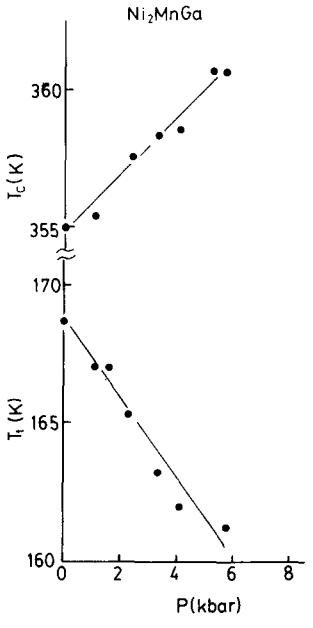

Fig. 6. The Curie temperature T_c and the structural phase transition temperature T_t vs. pressure curves for Ni_2MnGa.

determined in the present experiment are large in comparison with those reported by Austin and Mishra, and Kaneko et al. As the Curie temperatures are almost the same for each experiment, this discrepancy may be due to the calibration of pressure.

4. Discussion

The Heusler alloys Ni_2MnZ(Z = Al, Ga, In, Sn, and Sb) are typical metallic ordered alloys in which Mn atoms have definite localized moments of about $4\mu_B$. The paramagnetic susceptibility above the Curie temperature obeys the Curie–Weiss law, and the effective magnetic moment estimated from the Curie constant agrees satisfactorily with the saturation magnetic moment at the lowest temperature [10]. Since the nearest neighbour Mn–Mn distance is larger than 4.1 Å, the moments of Mn atoms are expected to be coupled via conduction electrons. So, the mechanism of the magnetic interaction in these alloys is thought to be an s–d exchange of RKKY type or of the double resonance type proposed by Caroli and Blandin [15]. The group of Ishikawa [16] has observed the spin wave of ferromagnetic Heusler alloys Ni_2MnSn, Pd_2MnSn and Cu_2MnAl by neutron inelastic scattering experiments. They determined the spin wave dispersion in these compounds by this technique and the exchange parameters were evaluated using a Heisenberg Hamiltonian. We consider that the most important conclusion in their studies is that the oscillatory nature of the s–d interaction was observed by direct means. Another important conclusion is that the exchange parameter between the nearest and next nearest neighbours, by which most of magnetic properties are determined, have the opposite sign to those expected in the RKKY type in the free electron model, and the Caroli and Blandin type interaction models. Furthermore, Endo [17] showed that the simple s–d type interaction gives a negative Curie temperature if it is calculated using the appropriate Fermi wave vector k_F and phase shift ϕ of the conduction electrons. Austin and Mishra [7] also reported that the simple s–d exchange model was inadequate to describe the exchange interaction in the Heusler alloys on the basis of their results on dT_c/dp. It seems that the pressure effect of the Curie temperature of Ni_2MnZ observed in this experiment may not be explained by the simple s–d exchange, and Caroli and Blandin models. So, we discuss qualitatively the interatomic distance dependence of the exchange interaction of Ni_2MnZ.

Castelliz [2] has proposed an empirical curve, in which the Curie temperature of ferromagnetic manganese alloys are plotted against the ratio of the nearest interatomic distance between manganese atoms to the radius of manganese atom (R/d). The curve has a maximum at about 3.6 of R/d. So, we can expect $dT_c/dp > 0$ for alloys located on the curve with $R/d > 3.6$. Kaneko et al. [8,9] reported that dT_c/dp is positive for the Heusler alloys ($L2_1$-type) Ni_2MnSn, Ni_2MnSb and $C1_b$-type alloys $Pt_{1-x}Au_xMnSb$ ($x = 0.4$ and 0.6) which have R/d larger than 3.6. The values of R/d for the present alloys are about 5.0. Positive dT_c/dp obtained for the present alloys is consistent with that expected from the above interaction curve. Fig. 7 shows the relationship of

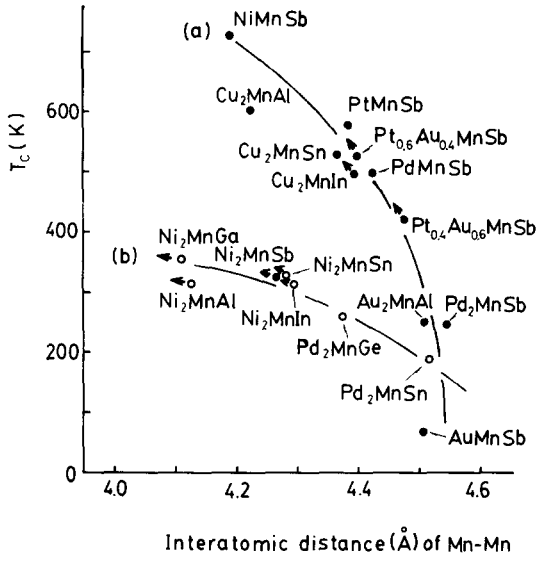

Fig. 7. The relation between the Mn–Mn distance and the Curie temperature for $L2_1$- and $C1_b$-type alloys.

the Mn–Mn distance to the Curie temperature for $L2_1$-type and $C1_b$-type alloys. A number of crystallographic and magnetic properties of the $L2_1$-type and $C1_b$-type alloys have already been studied and reviewed by a number of authors [10,12,18–20]. The alloys in which the main carriers of the magnetic moment are the Mn atoms are showed in the figure. We excluded the Heusler alloys Co_2MnZ(Z = Al, Si, Ga, Ge, Sn, and Sb) [21] and Rh_2MnZ(Z = Sn and Pb) [22] from the figure because it was reported that Co and Rh atoms carry the magnetic moments. In fig. 7, closed circles refer to the alloys in which the number of valence electron (the s–p electrons) per molecule in the alloys n is 6–7. Open circles refer to the alloys in which n is 4–5. The above value of n was deduced by assuming that the number of s–p electrons supplied may be zero from the Co and Ni families, one from each of the Cu family and Mn atoms, and three, four and five from IIIb, IVb, and Vb families, respectively. The arrows attached to the marks of the alloys in fig. 7 are the symbol to show the variation of the Curie temperature with pressure (the upward arrow expresses the rise of the Curie temperature). It is evident from the figure that the Curie temperatures of alloys with $n = 6$–7 tend to decrease sharply with increasing Mn–Mn distance. On the contrary, the Curie temperatures of alloys with $n = 4$–5 decrease gradually with increasing Mn–Mn distance. It is remarkable that the Curie temperature of both kinds of alloys ($n = 4$–5 and 6–7) depends strongly and definitely on the Mn–Mn distance, though it is widely accepted that the Curie temperature of $L2_1$- and $C1_b$-type alloys depends strongly on the number of valence electron. The emperical interaction curve proposed in this paper predicts that the presssure derivative of the Curie temperature should be positive for the present alloys. In fact, the positive pressure derivative of the Curie temperature was observed as descrived above. This interaction curve is supported also by the fact that the pressure derivative of the Curie temperature of Cu_2MnIn [6] and $Pt_{1-x}Au_xMnSb$ ($x = 0.4$ and 0.6) [9] is everywhere positive as shown in fig. 7. The positive pressure derivative of the Curie temperature for the alloy Ni_2MnSb is consistent with the prediction mentioned above. However, the deviation of the Curie temperature from the curve (a) is not clear at the present. The study of a pressure effect on the Curie temperature of other alloys which have the $L2_1$- and $C1_b$-type structure is in progress.

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