Atomic Disorder, Magnetic property and Thermal vacancy formation Co based Heusler Alloys Co_2MnZ (Z=Si, Ge, Sn)

Inamul Haq Wani [1], Aayushi Sharma[2], Indu Sharma[3], Mohd Shafiq[4], Brij Bir Singh[5], Sushila[6]

Department of Physics, Vivekananda Global University Jaipur, Rajasthan, India[1, 6]

Department of Physics Maulana Azad Memorial College, Jammu, Jammu and Kashmir, India [2,3,4,5]

Corresponding Author: Inamwani123@gmail.com

Keywords: Full Heusler Alloys, Magnetic Properties, Atomic Disorder, Thermal Vacancy

ABSTRACT:-

Co type and MnZ type at atomic and magnetic disorder are investigated for Co based Heusler alloy Co2MnZ (Z=Si, Ge, SN) as a function of quenching temperature. It is shown that Co type disorder preferentially proceeds with increase in quenching temperature while the MnGe type disorder preferentially proceeds in Co2MnGe. In Co2MnSn only the Mn-Sn type disorder proceeds. On the other hand decrease with in quenching temperature Co2MnGe, while it remains almost constant Co2MnSn.

1. INTRODUCTION:-

Co-based heusler type ferromagnetic alloys with the chemical formula X_2YZ(where X=Co),y=(Cr and Mn) and (Z=Si,Ge,Sn and Al) such as Co2CrSi ,Co2MnGe and Co2CrAl are prospective candidate for application in the spin electronic devices because these are theoretical prediction to be half metal ferromagnets with 100% spin polarization due to a gap at the Fermi level is the minority spin band .Despite the theoretical prediction it is difficult demonstrate the half metalicity for these compounds. Some factors such as atomic disorder, nonstoichiometry and oxidation in the bulk and oxidation in the bulk and interface are thought to leave degradation of the half metalicity. The heusler (L_{21}) (Co_2YZ) type structure with having four FCC

sublattices shown in fig1. It can also be regarded as the structure consisting of 8 BCC position in unit cells occupied the corner position. Co-sites are occupied by Co atoms by 8 bcc position are occupied alternatively Y atoms (Y site) and Z atoms (Z sites). Atomic disorder occurs by deviating the composition from the stiochiometry or by elevating temperature from 0k. Effect of the atomic disorder on the magnetic property as well as half metalicity in half heusler alloys Co_2YZ

As we studied half heusler alloy and full heusler alloy leads to the former type of disorder is predicted to lead the degradation of magnetism as well as half metalicity as the latter type does not significiantly affect the properties A degree of atomic disorder can be well controlled by quenching from appropriate temperature because it varies depending on temperature T. We have studied experiment magnetic behavior and atomic disorder in B2-type $Co_{1-x}Fex$ alloys ($0.4<x< 0.6$) and B_2 and heusler type $CoFe_{1-x}Al_x$ alloys ($0<x<1$) by quenching them for various temperature. This basically gives the relationship between atomic disorder and magnetism. As a result it is shown that atomic disorder at Co type disorder leads to degradation of magnetism in heusler phase. In B_2-phase $Co_{1-x}Fex$ and $CoFe_{1-x}Al_x$ alloys it was that proceeding of atomic disorder on Co site, Co-type disorder leads to a certain decrease in their mean magnetic moment. On the other hand, heusler phase $CoFe_{1-x}Al_x$ alloys around the stoichiometry composition Co_2FeAl ($x=0.5$) it was that the mean magnetic remains almost constant irrespective of atomic disorder between the Fe atomic disorder between the Fe and Al sites. Therefore this type of disorder affects hardly the magnetism. It is an intresting subject to clarify such a role of atomic disorder on the magnetism in various alloys Co_2MnGe. In this work however one problem remains to be solved namely about the change in lattice constant (a) with quenching temperature, T_Q in fig2 shows a result for these alloys. The lattice constant decrease with increase in temperature up to 1073k Co_2MnSi while Co_2MnGe rather slowly in the form of former and steeply in the latter, while in Co_2MnSn it shows a steep decrease up to 1273k. Further an anomalous change in (a) occur in Co_2MnSi, Co_2MnSi, and Co_2MnGe. Therefore the curve shows an inflection above 1073k.

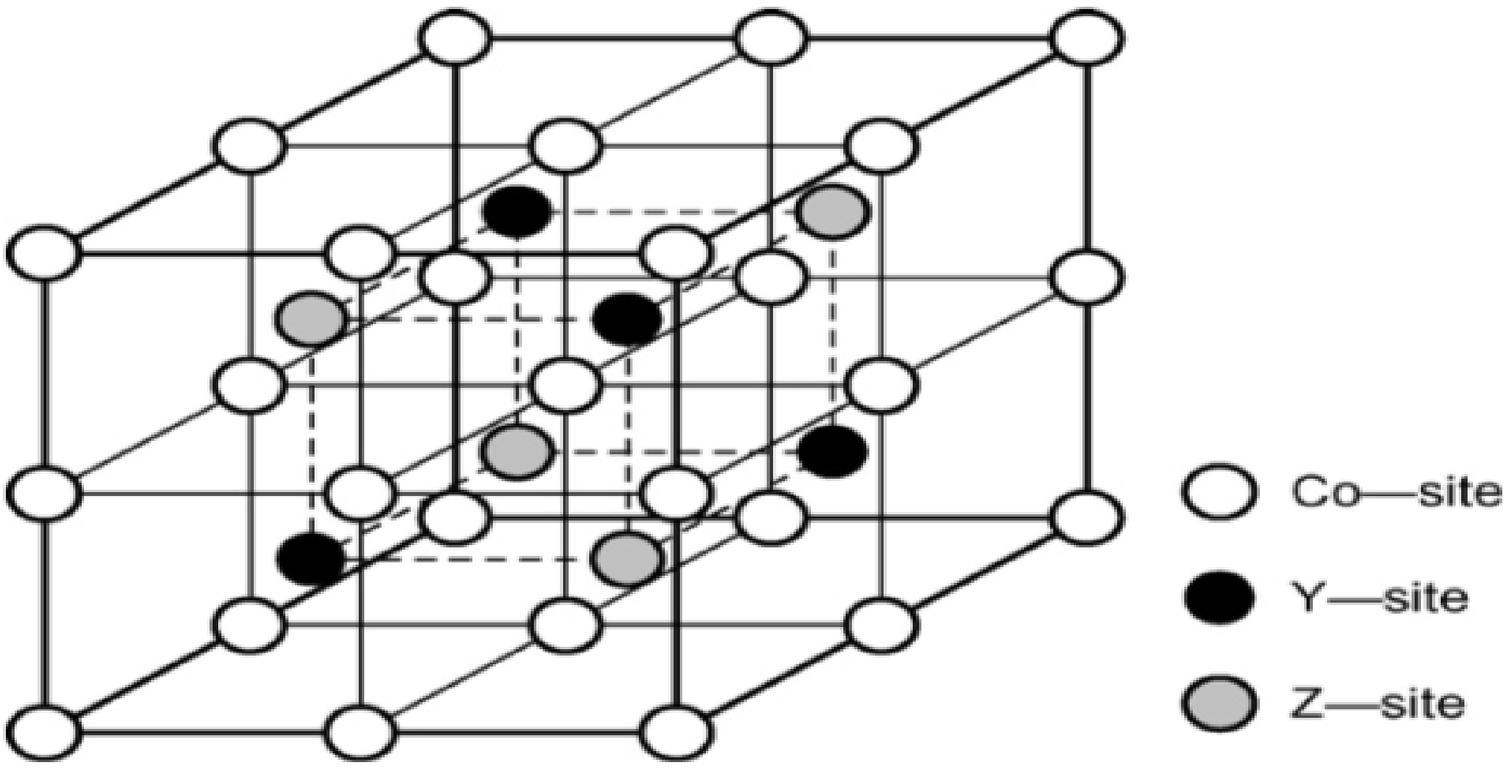


Fig. 1. Co_2YZ Heusler ($L2_1$)-type ordered structure.

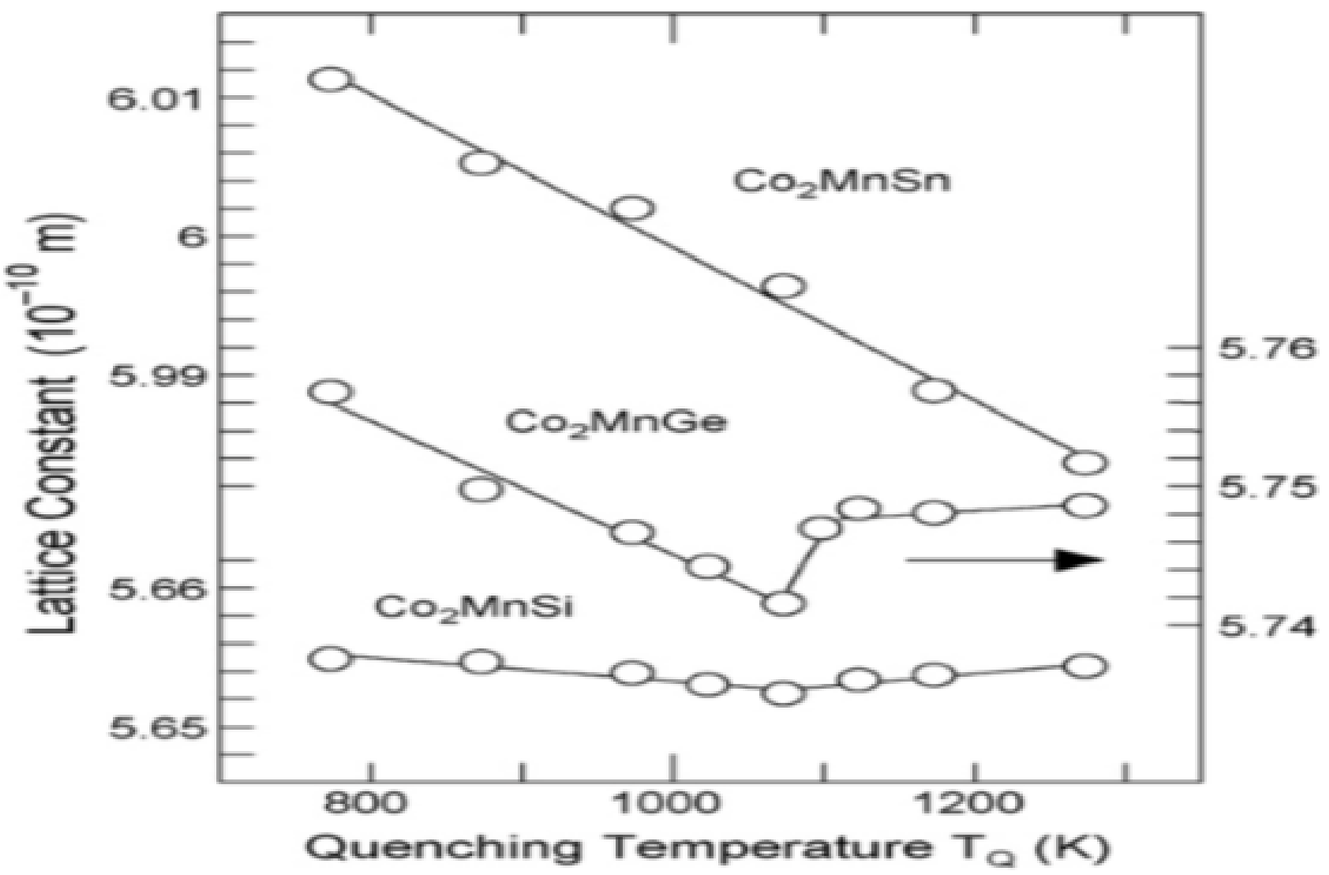


Fig. 2. Quenching temperature dependence of the lattice constant a in Co_2MnSi, Co_2MnGe and Co_2MnSn alloys. These data are quoted from Ref. [10].

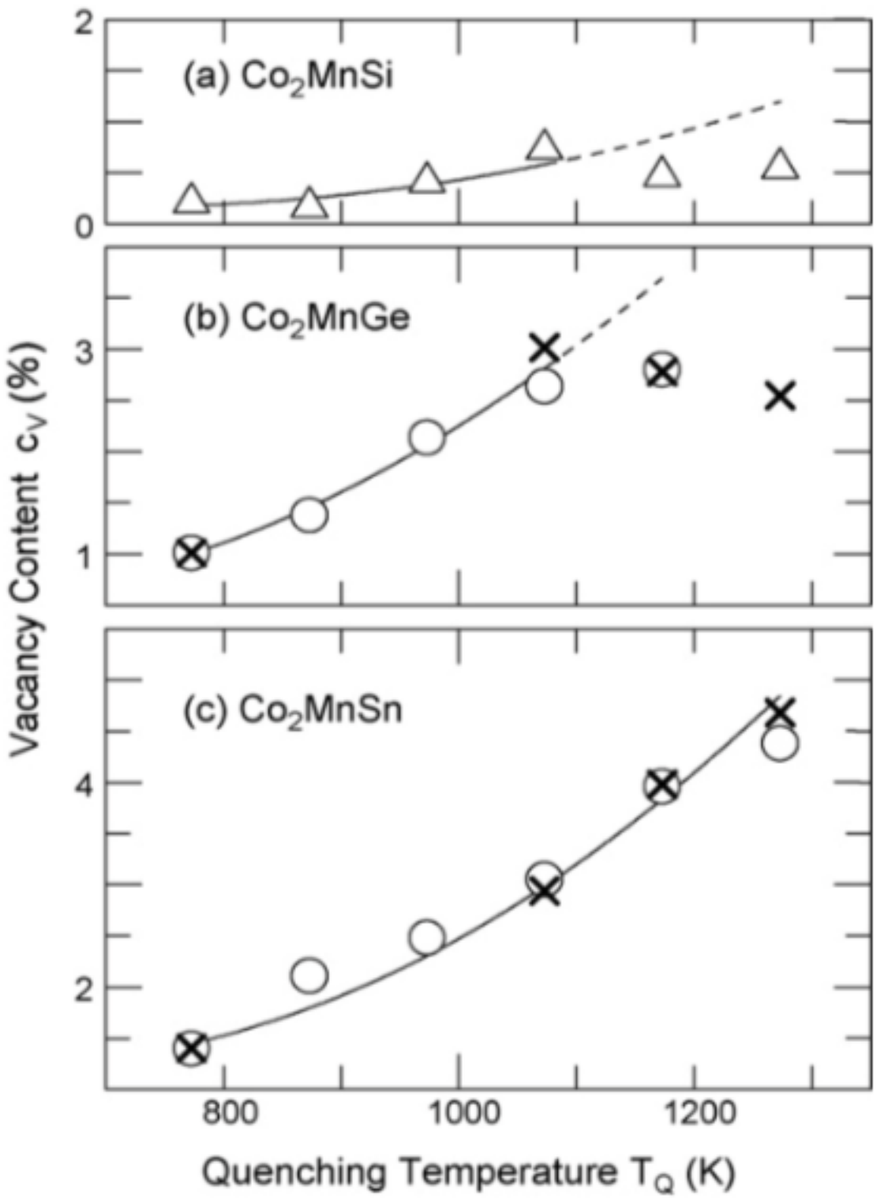
2. Experimental procedures

Co2MnZ (Z = Si, Ge and Sn) alloys were prepared by arc melting Co and Mn (purity of 99.99%) and Si, Ge and Sn (99.999%). Weight losses were less than 0.5%. Each ingot was homogenized at 1273 K for 50 h in a sealed silica tube filled with argon. The plate samples with a size of about 10 mm × 5 mm × 1 mm were prepared for density measurement. They were annealed at 1173 K for 2 h in silica tubes filled with argon, followed by cooling to room temperature at a rate of 2 K/min. Individual samples were again annealed at

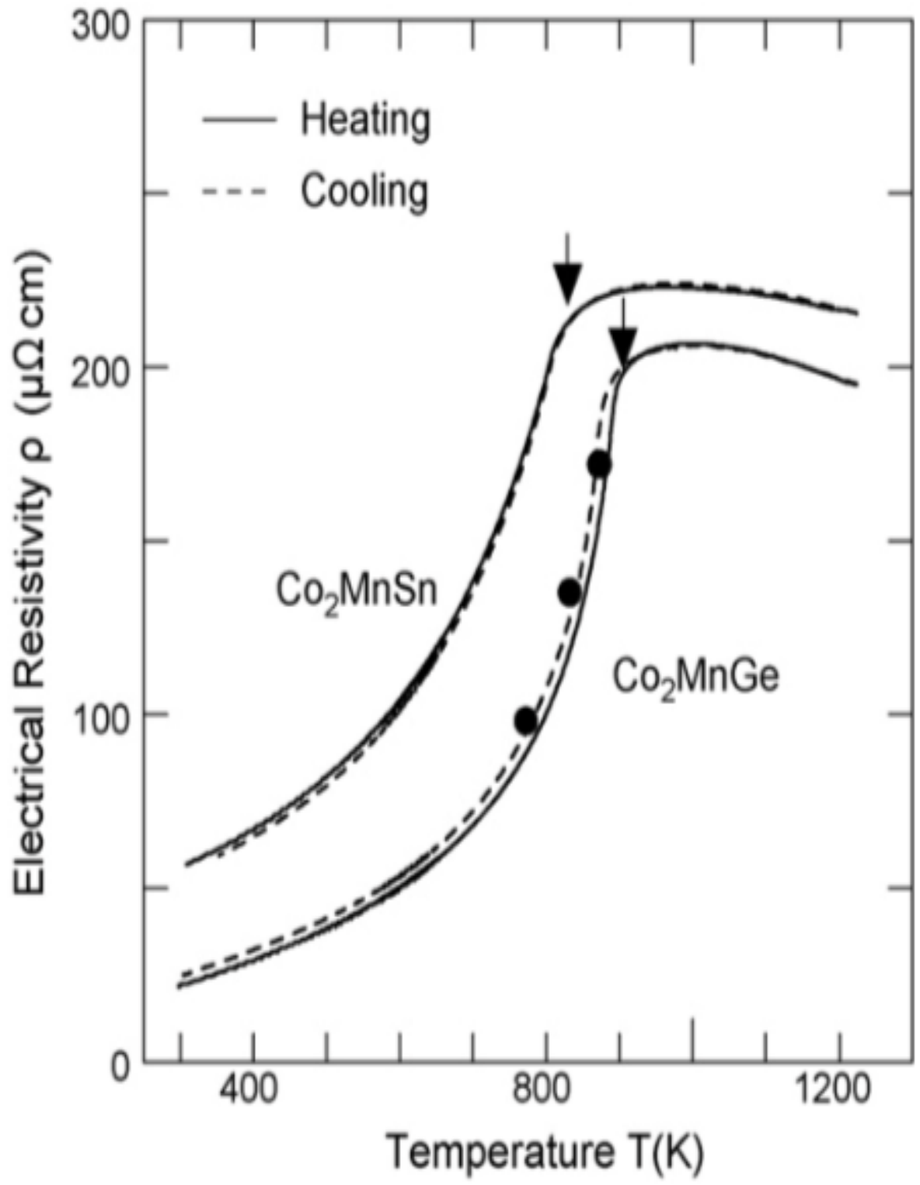
various temperatures from 773 K to 1273 K and then water-quenched (in quenching from temperatures above 973 K, the silica tubes were immediately crushed in water). Quenching temperature TQ and holding time are, 773 K (25–50 d), 873 K (14–21 d), 973 K (5–7 d), 1073 K (24 h), 1173 K (5 h) and 1273 K (1 h). The density measurement was performed based on the Archimedes method using distilled water in the same way as described. The vacancy concentration, Cv, can be obtained from

$C_v = NV/ N + NV = d_x - d_{obs}/ d_x$.

The deviations of Cv (%) were 1.2% in Co2MnGe and 0.3% in Co2MnSn. Consequently, for all the Cv data by the plate first water-quenched from 1173 K in a similar way as in the density measurement (without crushing silica tube) and then, after heated from room temperature to 773 K at a rate of


(a) Co2MnSi
(b) Co2MnGe
(c) Co2MnSn
Vacancy Content cV (%)
2
0
3
1
4
2
800
1000
1200
Quenching Temperature TQ (K)

about


300
Heating
Cooling
200
100
0
Co2MnSn
Co2MnGe
400
800
1200
Temperature T(K)

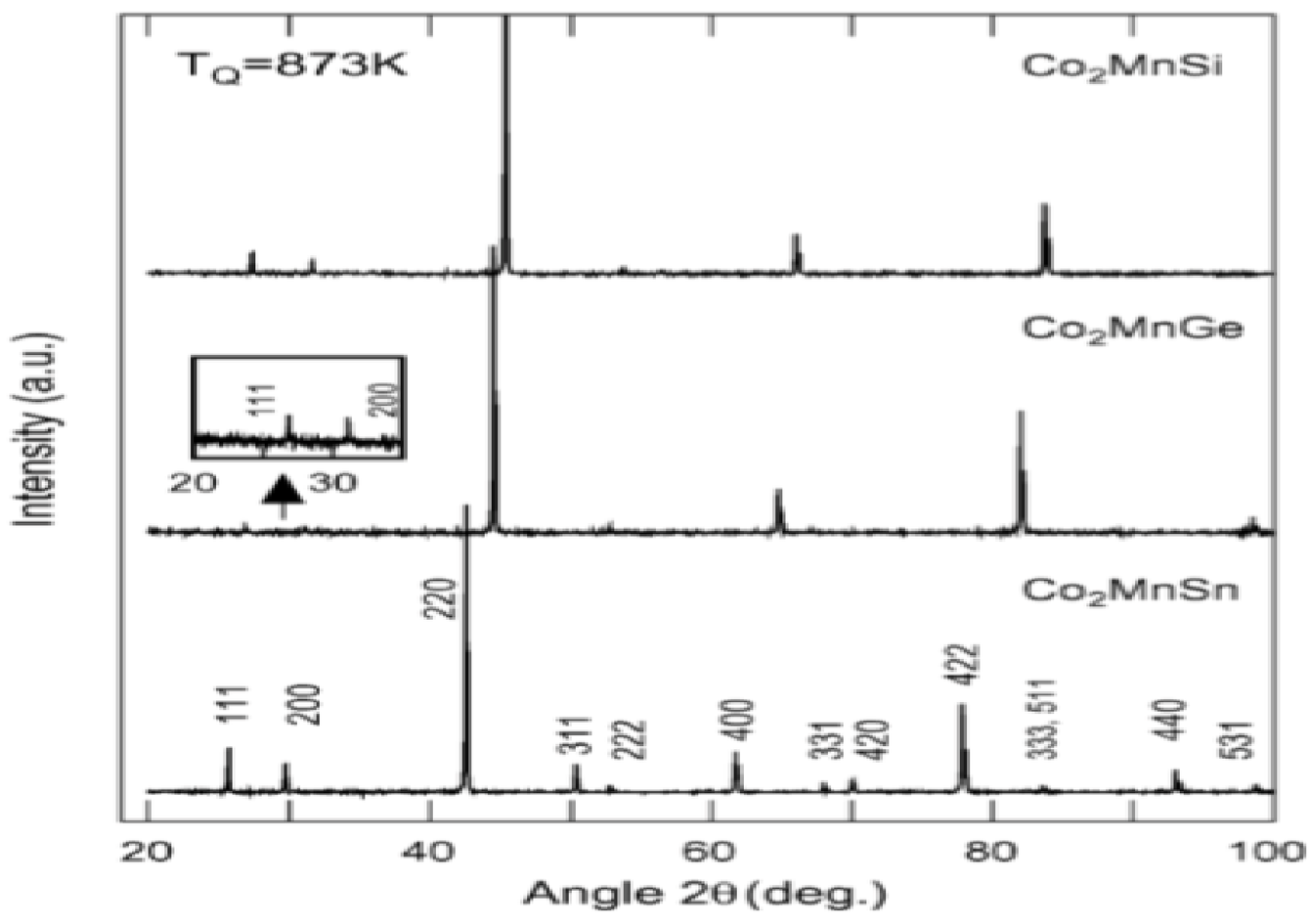
70K/min,the measurement was started.

Further, the other plate samples (about 5 mm × 5 mm × 1 mm) for positron annihilation measurements were prepared for Co2MnSi, Co2MnGe and Co2MnSn. As reference samples, plate samples of pure Co, Mn, Si, Ge and Sn were also prepared for the CDB measurement. The positron lifetime and CDB spectra consisted of 1.0 × 106 and more than 109 counts, respectively.

2.2. Procedure for atomic disorder determination

2 .2.1. Definition of the LRO-parameters and the Co-type and Y–Z-type defect concentrations

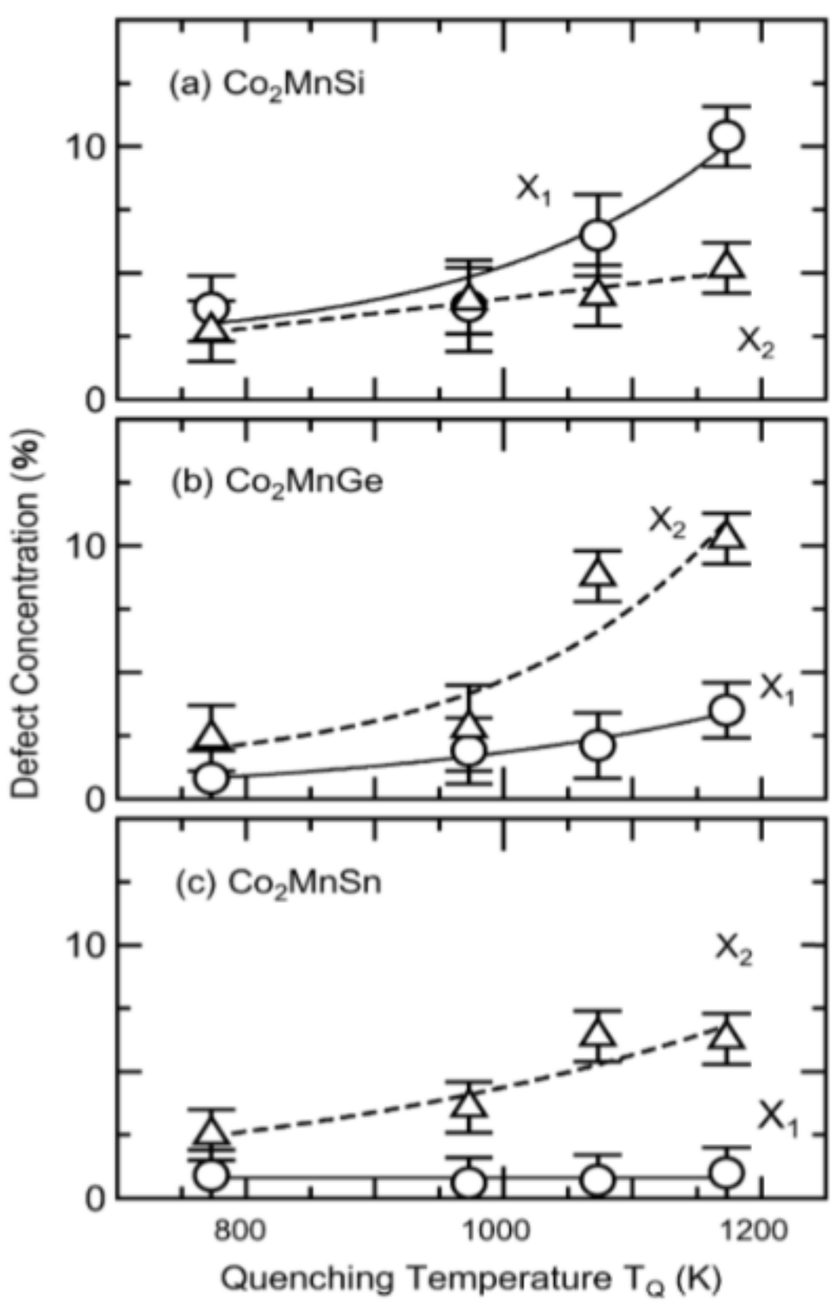
The point defect structure in the Co2YZ-type Heusler alloy can be described by specifying nine concentrations of constituent atoms on respective sites: three for the right atoms, e.g., Co atom on the Co-site, and six for the antisite atoms, e.g., Y atom on the Z-site and Z atom on the Y-site. Among these, number of the independent variables is four, so that four long-range order (LRO) parameters are generally needed for description of the defect structure. Here, for simplicity, we will follow the defect model adopted in our previous studies for CoFe1−xAlx Heusler alloys, which is based on the model proposed by Webster in neutron diffraction study. Then, the number of the LRO-parameters is reduced to two.

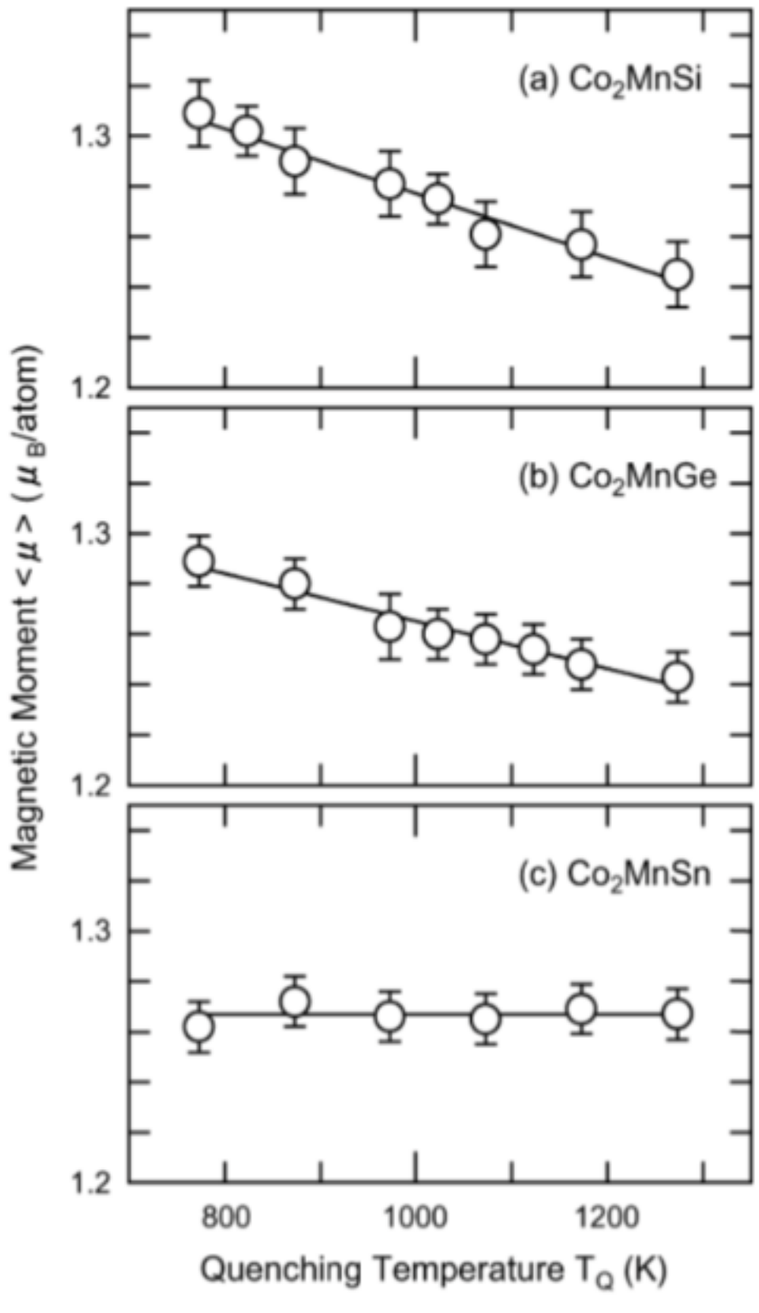


3. Results

3.1. Lattice constant

The quenching temperature dependence of the lattice constant, a, is shown by the open circles in Fig. 4 for Co2MnSi in Fig. 4(a), Co2MnGe in Fig. 4(b) and Co2MnSn in Fig. 4(c). The lattice constant shows a decrease with increase in quenching temperature TQ up to 1073 K in both alloys Co2MnSi and Co2MnGe. The slope is however, very gradual for the former and steep for the latter. In Co2MnSn, it decreases steeply (nearly the same slope as in the Co2MnGe) up to 1273 K. Two cross marks at TQ = 773 K and 1073 K in Fig. 4(a) represent the data by Ravel et al. [14]. Agreement with the present results is good. Further, the values of a reported by Webster are close to the present data at 973 K in Fig. 4(a)–(c). Another feature to be noted in Co2MnSi (Fig. 4(a)) and Co2MnGe (Fig. 4(b)) is that anomalous change in the lattice constant occurs, i.e., the curves show an inflection above 1073 K.





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3.2. Atomic disorder

Fig. 5 shows the quenching temperature dependence of the defect concentrations X1 (open circles) and X2 (open triangles) for Co2MnSi in Fig. 5(a), Co2MnGe in Fig. 5(b) and Co2MnSn in Fig. 5(c). Both defect concentrations are found to increase with increase in quenching temperature in Co2MnSi and Co2MnGe. However, in Co2MnSi, the slope is rather steep in X1 than in X2 and thus, the concentration X1 becomes much higher than X2 at higher quenching temperatures (TQ > 973 K), while just reversed situation is recognized in Co2MnGe. Namely, it can be said that the Co-type disorder preferentially proceeds in Co2MnSi alloy as the quenching temperature increases, whereas in Co2MnGe alloy, the Mn–Ge-type disorder preferentially proceeds. On the other hand, in Co2MnSn alloy, X1 is very small and remains almost constant and so, only the Mn–Sntype disorder occurs in practice. The same behavior was also observed in Heusler-phase CoFe1−xAlx alloys (0.4 ≤ x ≤ 0.6). Webster and Brown et al. have studied the atomic disorder in present Heusler alloys by neutron diffraction measurement. According to their results, Co2MnSi and Co2MnSn alloys are highly ordered (X1 = X2 ≈ 0%), but a small degree of disorder between the Mn- and Ge-sites (X2 ≈ 4%) is detected in Co2MnGe alloy . These results correspond fairly well to the present observation at lower quenching temperatures (TQ ≤ 973 K), although the present X1 and X2 are somewhat larger in Co2MnSi (Fig. 5(a)). Further, Rabel et al. obtained the defect concentrations for Co2MnSi alloys quenched from 773 K and 1073 K by neutron diffraction measurement. The results were, X1 = 6.9% and X2 = 0% at TQ = 773 K and X1 = 7.4% and X2 = 0% at TQ = 1073 K. Their results of X2 = 0% come from the situation that all the Si-sites are exclusively occupied by Si atoms. Thus, the change in X1 mentioned above is due to proceeding of disorder between the Co- and Mn-sites (Co–Mn-type disorder). When only this type of disorder occurs, ordinary X-ray diffraction method, used in the present study, cannot give any information because of the small difference in atomic scattering factors between Co and Mn atoms. However, it can give rather correct information about the concentrations of the antisite Co and Mn atoms on the Si-site (xSi Co and xSi Mn). Our results showed that e.g., the concentration xSi Co increases certainly from 3.6% at TQ = 773 K to 10.4% at TQ = 1173 K,

resulting in the changes in X1 and X2 shown in Fig. 5(a) (cf. Fig. 3(a)). The reason of this discrepancy is not clear, although it may come from the difference in some factors relating to the experimental method and the sample preparation.

3.3. Mean magnetic moment

The quenching temperature dependence of the mean magnetic moment is shown by the open circles in Fig. 6 for Co2MnSi in (a), Co2MnGe in Fig. 6(b) and Co2MnSn in Fig. 6(c). The magnetic moment decreases with increase in quenching temperature in Co2MnSi and Co2MnGe, rather gradually for the latter compared with the former. On the other hand, in Co2MnSn, remains almost constant. Webster has previously measured the magnetic moment for various Co2MnZ alloys. Obtained values of are 1.27 for Co2MnSi and Co2MnSn and 1.28 for Co2MnGe in atom unit, which are close to the present results at TQ = 1023 K for Co2MnSi and at TQ = 873 K for Co2MnGe and, agree well with that for Co2MnSn.

3.4. Vacancy concentration

The quenching temperature dependence of the vacancy concentration Cv is shown in Fig. 3 for Co2MnSi in (a), Co2MnGe in (b) and Co2MnSn in (c). The open triangles and cross-marks represent the results obtained for the plate samples and the powder samples, respectively. As mentioned in previous section, the plate sample data are corrected for Co2MnGe and Co2MnSn, which are plotted by the open circles (Fig. 3(b) and (c)). Agreement with corresponding powder sample data is good. The solid and dotted curves represent the fitting curves, which are mentioned in later Section 3.4.1. The vacancy concentration Cv increases with increase in quenching temperature TQ up to 1073 K in Co2MnSi and Co2MnGe and up to 1273 K in Co2MnSn. The slope is rather gradual for Co2MnSi, while very steep for Co2MnGe and Co2MnSn, corresponding well to the observed trend in the lattice constant a shown in Fig. 2. Furthermore, in Co2MnSi (Fig. 3(a)) and Co2MnGe (Fig. 3(b)), reduction of Cv values from the dotted curves is recognized above 1073 K, which just corresponds to the inflection found in a of these alloys (Fig. 2).

Therefore, it can be said that there is a certain correlation between changes in the vacancy concentration and the lattice constant in the present Heusler alloys.

3.5. Electrical resistivity

Prior to the ageing experiment, we have measured the change in electrical resistivity, with temperature, T, for Co2MnGe and Co2MnSn, at heating and cooling rates of 2 K/min. The results are shown in Fig. 4 by the solid curves (heating process) and dotted ones (cooling process). In both alloys, an inflection is clearly found, which will be due to a magnetic transition since the inflection points are close to the Curie temperature, TC, shown by the arrows. A feature to be noted is that the resistivity shows a slight decrease after reaching its maximum above TC. Such a negative temperature dependence of in a range T > Tc has been already reported in some D03-type ferromagnetic ternary alloys (Fe1−xMx) 3X (e.g., X = Ga and Si, and M = Ti and V).

4. Conclusion

The Co-type and Mn–Z-type atomic disorder ,the magnetic behavior and thermal vacancy were studied for three Heusler-type ferromagnetic alloys Co2MnZ (Z = Si, Ge and Sn) as a function of quenching temperature. Concluding remarks are as follows:

(1) Both the Co-type and Mn–Z-type defect concentrations increased with increase in quenching temperature in Co2MnSi and Co2MnGe. However, the change in the former is rather steep than in the latter in Co2MnSi, while the reversed situation is found in Co2MnGe. Namely, the Co-type disorder preferentially proceeds in Co2MnSi, while the Mn-Ge-type disorder preferentially proceeds in Co2MnGe. In Co2MnSn, only the Mn-Sn-type disorder proceeds in practice.

(2) The mean magnetic moment decreased with increase in quenching temperature for Co2MnSi and Co2MnGe, while it remained almost constant in Co2MnSn.

(3) Relation between the atomic disorder and the magnetic behavior was examined. It is concluded that the Co-type disorder leads to degradation of the magnetism as observed in Co2MnSi and Co2MnGe, while the Mn–Z-type disorder affects hardly the magnetism as in Co2MnSn.

(4) The vacancy concentration determined from the density and lattice constant measurements increased with increase in quenching temperature up to 1073 K or 1273 K.

(5) Change in the electrical resistivity due to ageing at various temperatures of 773–873 K showed a relaxation behavior in Co2MnGe and Co2MnSn. This is due to annealing-out of the excess vacancies retained during furnace-cooling from 1173 K.

References

[1] Y. Miura, K. Nagao, M. Shirai, Phys. Rev. B69 (2004) 144413.

[2] S. Picozzi, A. Continenza, A.J. Freeman, Phys. Rev. B69 (2004) 094423.

[3] Y. Miura, M. Shirai, K. Nagao, J. Appl. Phys. 99 (2006) 08J112.

[4] I. Galanakis, K. Ozdogan, B. Aktas, E. Sasioglu, Appl. Phys. Lett. 89 (2006) 042502.

[5] K. Harada, H. Ishibashi, M. Kogachi, Mater. Res. Soc. Symp. Proc. 753 (2003), BB5.28.1.

[6] M. Kogachi, S. Minamigawa, K. Nakahigashi, Acta Metall. Mater. 40 (1992) 1113.

[7] M. Kogachi, T. Tanahashi, Scripta Mater. 35 (1996) 849.

[8] R. Wurschum, C. Grupp, H.E. Schaefer, Phys. Rev. Lett. 75 (1995) 97.

[9] H.E. Schaefer, K. Bedula-Gergen, Defect Diff. Forum 143–147 (1997) 193.

[10] M.S. Wechsler, Acta Metall. 5 (1957) 150.

[11] A. Broska, J. Wolff, M. Franz, Th. Hehenkamp, Intermetallics 7 (1999) 259.

[12] M. Kogachi, High Temp. Mater. Process. 18 (1999) 269.

[13] H.E. Schaefer, Proceedings of the International Conference on Positron Annihilation, 1985, p. 448