CHAPTER II

HEUSLER ALLOYS

Heusler alloys are intermetallic compounds, and as such exhibit the chemical order characteristic of compounds whilst retaining the metallic lustre and high conductivity of metals. Their magnetic properties are similarly intermediate. Most known Heusler alloys are ferromagnetic, and some contain moments of unequal magnitude, but others have recently discovered in which antiferromagnetic order exists. Consequently Heusler alloys, and related intermetallic compounds, provide an opportunity for investigation of the effects of chemical order and on the magnetic exchange interactions that occur in solids.

II. 1 The Heusler Structure

Owing to its important bearing on the general theory of magnetism, the discovery of Heusler alloys excited considerable interest and lead to numerous further investigations. Heusler et al[2] measured the intensities of magnetization of several alloys in the copper - manganese - aluminum and copper - manganese - tin systems, and found maxima at the approximate compositions Cu_2MnAl and Cu_6Mn_3Sn. Ross and Gray[3] reinvestigated the copper - manganese - tin system and found a second, larger,

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(2) Heusler, F., Starck, W. and Haupt, E.,

    Verh. der deut. phys. Gesell., 5 (1903) 220

(3) Ross, A.D. and Gray, R.C., Proc. Roy. Soc. Edinburgh, 31 (1910) 85

maximum in magnetic intensity near the composition Cu_2MnSn. In addition, they showed that the magnetization is affected by heat treatment. Quenching from $580°C$ usually result in a marked reduction in magnetization. Take and Semm[4] made a systematic survey of magnetism in the copper - manganese - tin system and published magnetic contours showing two pronounced maxima, one at Cu_6Mn_3Sn and the other, and larger one, at Cu_2MnSn.

Young[5] investigated the structure of an alloy at the approximate composition Cu_2MnAl using X-ray powder diffraction techniques. He was able to show that the structure of the alloy depends upon its previous heat treatment. The weakly magnetic alloy that had been quenched from red hot was indexed as face-centred cubic (f.c.c.) with a lattice parameter 3.70 kX, and the more magnetic specimen as a mixture of f.c.c. together with body-centred cubic (b.c.c.) structure of lattice parameter 2.98 kX.

Potter[6] investigated the X-ray structure of single cry-stals of Cu_2MnAl and found that the alloy was b.c.c. with a lattice parameter 2.95 kX. However the presence of f.c.c. superlattice lines indicated the existence of plane of low scattering power, and he was

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(4) Take, E. and Semm, A. Verh. der deut. phys. Gesell., 16 (1914) 971-89

(5) Young, E., Phil. Mag., 46 (1923) 291-305

(6) Potter, H.H., Proc. Phys. Soc., 41 (1929) 135

able to show that the aluminum atoms were arranged on an f.c.c. superlattice of cell size 5.9 kX. He was unable to distinguish between the copper and the manganese atoms because of the small difference in atomic scattering factors.

Persson[7] working independently on a series of alloys of the form $(CuMn)_3Al$ came to same structural conclusions. In addition he showed that only alloys with manganese content more than 19% are ferromagnetic, and concluded that this amount was necessary to produce an f.c.c. manganese sublattice.

Bradley and Rodgers[8] investigated the alluminum Heusler alloy with the object of locating by direct experiment the positions of the manganese atoms, and to test whether the change in structure without change of composition would affect the ferromagnetic character of the alloy. An alloy at the composition $Cu_{2.2} Mn_{0.65} Al_{1.15}$ was investigated because it exhibited an almost complete change in structure with heat treatment. After annealing at 500°C and slow cooling, the structure corresponded to the δ $Cu_9 Al_4$ structure, and was practically non-magnetic. The same alloy, after quenching from 800°C, had a b.c.c. structure with an f.c.c. superlattice and was strongly ferromagnetic confirming that the magnetic properties of the alloy are structure dependent.

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(7) Persson, E., Z.Physik, 57 (1929) 115

(8) Bradley, A.J. and Rodgers, J.W., Proc.Roy.Soc. A, 144 (1934)
     340

Heusler,[9] working independently, derived the same structure and showed that the lattice parameter had a maximum value of 5.935 kX at the composition Cu_2MnAl. He also determined the magnetization after various heat treatments, and recorded a maximum value equivalent to 3.4 Bohr magnetons per Cu_2MnAl group.

The structure is best decribed in term of four interpenetrating f.c.c. sublattices A, B, C and D with coordinates,

A	B	C	D
0 0 0	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$\frac{3}{4}\frac{3}{4}\frac{3}{4}$
$0\ \frac{1}{2}\frac{1}{2}$	$\frac{1}{4}\frac{3}{4}\frac{3}{4}$	$\frac{1}{2}\ 0\ 0$	$\frac{3}{4}\frac{1}{4}\frac{1}{4}$
$\frac{1}{2}\ 0\ \frac{1}{2}$	$\frac{3}{4}\frac{1}{4}\frac{3}{4}$	$0\ \frac{1}{2}\ 0$	$\frac{1}{4}\frac{3}{4}\frac{1}{4}$
$\frac{1}{2}\frac{1}{2}\ 0$	$\frac{3}{4}\frac{3}{4}\frac{1}{4}$	$0\ 0\ \frac{1}{2}$	$\frac{1}{4}\frac{1}{4}\frac{3}{4}$

At the stoichiometric composition Cu_2MnAl, the A and C sites are occupied by Cu atoms, the B sites by Mn atoms and the D sites by Al. This arrangement corresponds to the Strukturbericht type $L2_1$. This is shown in figure 1.

The range of alloys known to have the Heusler structure
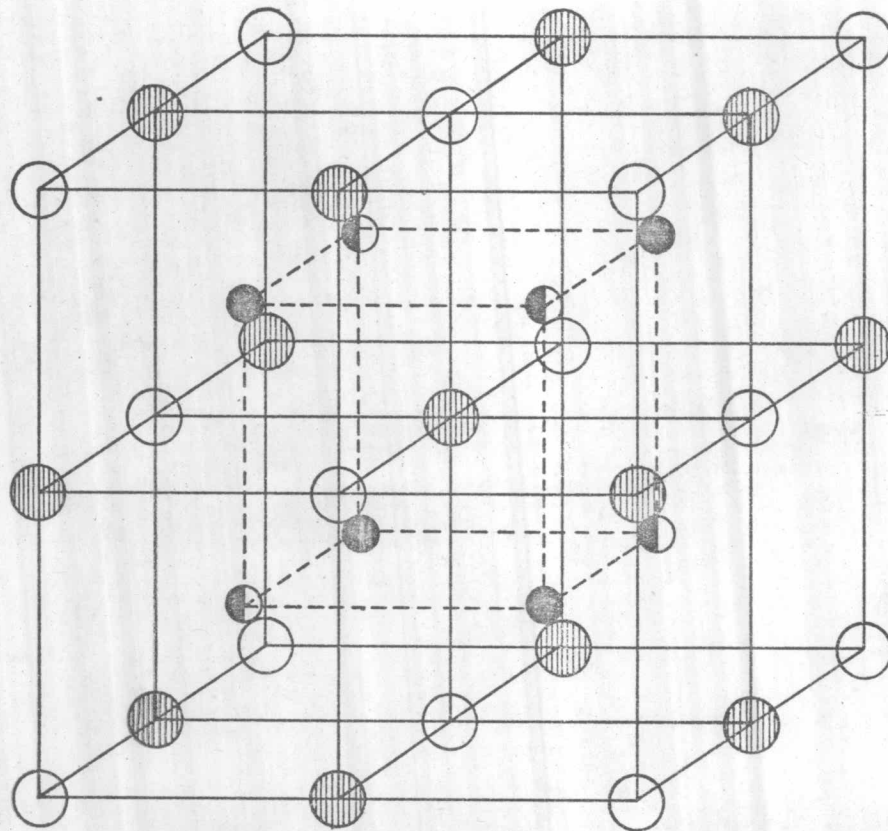
(9)   Heusler, O., Ann. Phys., 19 (1934) 155

Fig. 1   The Heusler, L2₁, structure.

has been extended in more recent times, and their structural and magnetic properties have been the subject of many investigations. Heusler alloys are now commonly defined as intermetallic compounds at the stoichiometric composition X_2YZ with the $L2_1$ structure. Results of the investigations are shown in table 1 (From 10, 11, 12 and 13).

II. 2   Chemical Order and the Heusler Structure

The chemical structure of the Heusler alloys is most readily determined using diffraction techniques. Originally X-ray diffraction was employed exclusively, but more recently, with the introduction of high flux nuclear reactors, it has become possible to perform neutron diffraction experiment also. No matter which technique is used the same geometrical considerations apply, and reinforcement of the diffracted beam occurs at

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(10)   Webster, P.J., Contemp. Phys., 10 (1969) 559

(11)   Szytula, A., INP report (Institute of Nuclear Physics, Cracow) No 808/PS (1972)

(12)   Masumoto, H. and Watanabe, K., J. Phys. Soc. Japan, 32 (1972) 281

(13)   Masumoto, H., Watanabe, K. and Ohnuma, S., J. Phys. Soc. Japan, 32 (1972) 570

Alloy	Lattice parameter (A°)	Tc $(^\circ K)$	Tn $(^\circ K)$	μ_B (Bohr magnetons)
Au_2MnAl	-	258	65	3.1
Cu_2MnAl	5.98	600	-	3.8
Cu_2MnIn	6.2	520	-	4.0
Cu_2MnSb	-	-	55	5.47
Cu_2MnSn	6.17	(530)	-	4.1
Ni_2MnGa	5.825	379	-	4.17
Ni_2MnSn	6.052	344	-	4.05
Ni_2MnSb	6.000	360	-	3.27
Co_2MnAl	5.756	697	-	4.01
Co_2MnSi	5.654	985	-	5.07
Co_2MnGa	5.770	694	-	4.05
Co_2MnGe	5.743	905	-	5.11

Table 1   A summary of the magnetic and structural properties of

Heusler alloys (From 10,11, 12 and 13)

Alloy	Lattice parameter (A°)	T_c $(^{\circ}K)$	T_n $(^{\circ}K)$	μ_B (Bohr magnetons)
Co_2MnSn	6.000	829	-	5.08
Pd_2MnAl	6.165	-	240	4.4
Pd_2MnIn	6.373	-	142	4.3
Pd_2MnSn	6.380	189	-	4.23
Pd_2MnSb	6.424	247	-	4.40
Pt_2MnGa	-	-	75	-
Pt_2MnAl	-	-	190	-
Ir_2MnGa	6.052	-	24	4.1
Ir_2MnAl	6.025	-	500	3.5
Rh_2MnGe	-	-	450	4.30
Rh_2MnAl	6.022	-	26	4.7

Table 1 (Continued)

A summary of the magnetic and structural properties of
Heusler alloys (From 10,11, 12 and 13)

angles Θ given by the Bragg equation,

$$2d_{hkl} \sin \Theta = \lambda \qquad (1)$$

where λ is the X-ray or neutron wavelength, and d_{hkl} is the spacing between the scattering planes. In the cubic system the separation of planes with Miller indices (hkl) is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad (2)$$

where a is the lattice parameter of the unit cell.

Not all combinations of h, k and l are possible to give reinforcement of the diffracted beam since for some destructive interference occurs between waves scattered from different locations in the unit cell. The generalized structure, described earlier, of four interpenetrating f.c.c. sublattices A, B, C and D gives rise to non-zero Bragg reflections only when the Miller indices of the scattering planes are either all even, or all odd. The even planes may be subdivided into two groups, those for which (h + k + 1)/2 is odd, and those for which (h + k + 1)/2 is even. The intensities of these reflections are determined by the square of the structure factors, F, which for the three types of reflection may be shown to be,

$$h, k, l = odd \qquad F = \left| 4 \left[(b_A - b_C)^2 + (b_B - b_D)^2 \right]^{\frac{1}{2}} \right|$$

$$(h + k + l)/2 = 2n + 1 \qquad F = \left| 4 \left[b_A - b_B + b_C - b_D \right] \right|$$

$$(h + k + l)/2 = 2n \qquad F = \left| 4 \left[b_A + b_B + b_C + b_D \right] \right|$$

$$(3)$$

where b_A, b_B, b_C and b_D are the average scattering amplitudes or scattering length for the A, B, C and D sites respectively.

F (111) and F (200) contain difference terms and hence correspond to the order-dependent superlattice reflections which would be absent if all the average scattering amplitude are equal. F (220) is the sum of the scattering amplitudes and is independent of order. Such reflections are known as the principal reflections.

In an ordered Heusler alloy X_2YZ, X atoms occupy the A and C sites, Y atoms the B sites and Z atoms the D sites. Substitution of b_x, b_y and b_z, the respective scattering amplitudes into equation (3) gives the structure factor for a Heusler alloy,

$$F \ (111) \qquad = \quad 4 \left| b_y - b_z \right|$$

$$F \ (200) \qquad = \quad 4 \left| 2b_x - (b_y + b_z) \right|$$

$$F \ (220) \qquad = \quad 4 \left| 2b_x + (b_y + b_z) \right| \qquad (4)$$

In binary alloys, it is convenient to define an order parameter

S which infer some of the important features of the configurational state. In particular, the intensities of binary superlattice reflections are proportional to S^2.

It is not possible to describe the state of ternary alloys with only one order parameter, except in special cases such as when the disorder is perfectly random. In practice, the probability of one type of atomic disordering is not equal to that of another, and then a set of ordering parameters is required. The amount of disorder may be represented by a disordering parameter, α, which for a Heusler alloy is defined as the fraction of either Y or Z atoms not on their correct sublattices.

Table 2 illustrates seven such ways in which an alloy at the Heusler composition X_2YZ might be arranged on four interpenetrating f.c.c. sublattices.

(1) is the correct arrangement of atoms in the Heusler structure.

(2) and (4) represent a departure from the $L2_1$ arrangement if disorder occurs between only one of the X sublattices and either the Y or Z sublattice, respectively. If disorder of this type proceeds, the initial state of order is replaced by another state of order, reached when $\alpha(2,4) = 1$. If this state of order is reached, X atoms will occupy adjacent sublattices, B and C say, and the Y and

Type of disorder	Sublattice A	Sublattice B	Sublattice C	Sublattice D
1 Complete $L2_1$ order	X	Y	X	Z
2 (X-Y) disorder	$(1-\alpha)X + \alpha Y$	$(1-\alpha)Y + \alpha X$	X	Z
3. (X-Y-X) disorder	$(1-\frac{\alpha}{2})X + \frac{\alpha}{2}Y$	$(1-\alpha)Y + \alpha X$	$(1-\frac{\alpha}{2})X + \frac{\alpha}{2}Y$	Z
4 (X-Z) disorder	$(1-\alpha)X + \alpha Z$	Y	X	$(1-\alpha)Z + \alpha X$
5 (X-Z-X) disorder	$(1-\frac{\alpha}{2})X + \frac{\alpha}{2}Z$	Y	$(1-\frac{\alpha}{2})X + \frac{\alpha}{2}Z$	$(1-\alpha)Z + \alpha X$
6 (Y-Z) disorder	X	$(1-\alpha)Y + \alpha Z$	X	$(1-\alpha)Z + \alpha Y$
7 (X-Y-X-Z) disorder	$(1-\frac{2\alpha}{3})X + \frac{\alpha}{3}(Y+Z)$	$(1-\alpha)Y + \frac{\alpha}{3}(2X+Z)$	$(1-\frac{2}{3}\alpha)X + \frac{\alpha}{3}(Y+Z)$	$(1-\alpha)Z + \frac{\alpha}{3}(2X+Y)$

Table 2   The arangements of atoms of an alloy X_2YZ on four interpenetrating f.c.c. sublattices A, B, C and D.

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z Z atoms will be on the A and D sublattice respectively.

(3) and (5) represent a state of disorder between any X sites, and either the Y or Z sites. Maximum disorder of this type occurs when α (3,5) = 0.75 but again this is the condition for complete order of another form.

(6) is the atomic arrangement when the X atoms remain ordered and disorder occurs between Y and Z sites only. Maximum disorder of this type occurs when α (6) = 0.5.

(7) is the atomic arrangement when random disorder occurs. Complete disorder occurs when α (7) = 0.75 a state that is equivalent to that represented by the binary ordering parameter S = 0.

Utilization of both neutron and X-ray diffraction data is usually sufficient to determine unambiguously the state of chemical order in any Heusler alloy. The neutron data are normally used to determine quantitatively the degree and type of disorder, if any, and the X-ray data used for qualitative confirmation and elimination of possible ambiguities. There are two main reasons for this. Firstly, the intensities of neutron diffraction peaks may be determined in general with much greater accuracy than those of the corresponding X-ray peaks, because with neutron absorption corrections are usually negligible, whereas with X-rays they are

considerable, and vary rapidly and in a complicated manner with Bragg
angle. Secondly, the scattering lengths are often more favourable.
This is because the scattering of X-rays is due to their electro-
magnetic interaction with the electron clouds of the atoms, whereas
the nuclear scattering of neutrons is a direct interaction with the
nucleus. Consequently X-ray scattering amplitudes increase steadily
with atomic number, and it is difficult to distinguish between elements
close together in the periodic table. In addition, since all X-ray
scattering amplitudes have the same algebraic sign, superlattice
lines tend to be much weaker than the principal lines. The neutron
scattering amplitude is usually expressed in terms of a scattering
length b, determined by the boundary conditions at the surface of
the nucleus. In contrast to X-rays b does not increase steadily
with atomic number but behaves erratically, taking both positive
and negative values, and different values for different isotopes.
Consequently adjacent elements in the periodic table may often be
distinguished using neutrons. In addition, intermetallic compounds
containing elements with scattering lengths of different sign will
have superlattice line intensities comparable to the principal line
intensities. This is fortunately the case with most Heusler alloys
since manganese, the most common constituent, has a negative scat-
tering length, whereas all other constituents have positive scat-
tering lengths. Thus manganese, which is difficult to distinguish
from other transition metal elements using X-rays, is particularly

easy to locate using neutrons.

The ordering of the manganese atoms in the Cu_2MnAl structure was established by Bradley and Rodgers[8] and by Heusler[9] in 1934 using X-rays. Confirmation of the fully ordered Heusler structure of Cu_2MnAl was provided by Felcher, Cable and Wilkinson[14] by means of neutron diffraction in 1963. In 1968 Johnston and Hall[15] reinvestigated the Cu_2MnAl alloy using both X-rays and neutron diffraction. These authors were able to establish the state of disorder of the alloy after being treated at different temperature with different time.

II. 3   Magnetic Order and the Heusler Structure

It was established by the early investigators that the chemical structure of the Heusler alloys is important in determining the magnetic properties, and it was believed that the manganese ions carried the magnetic moment. The first direct evidence in support of this view was obtained by Felcher et al [14] from neutron diffraction measurements.

Felcher et al investigated the magnetic moment distribution in the Heusler alloy Cu_2MnAl, using a large magnetic field to

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(14)   Felcher, G.P., Cable, J.W. and Wilkinson, M.K., J. Phys. Chem. Solids, 24 (1963) 1663

(15)   Johnston, G.B. and Hall, E.O., J.Phys. Chem. Solids, 25 (1968) 193

separate the magnetic and nuclear scattering contributions. They were able to show that within the accuracy of the experiment the entire moment of the molecule could be attributed to the manganese atom. Later experiments[16] have confirmed that in most Heusler alloys containing manganese the magnetic moment is confined to the manganese sites and is usually 4 Bohr magneton per atom. The only known exceptions are a series containing cobalt[10] in which the magnetic moment is shared between the manganese and cobalt atoms.

Magnetic ordering in most Heusler alloys containing manganese was established by neutron diffraction measurements. It was found that, with fully ordered $L2_1$ structure, magnetic moments carried by manganese ions are coupled ferromagnetically along one of the crystallographic axes. When partial disorder occurs by which some part of the manganese atoms are situated not on their proper site, their magnetic moment will be coupled ferromagnetically with each other but antiferromagnetically with those on the B site.[17]

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(16) Webster, P.J., Phil. Mag., 16 (1967) 347

(17) Natera, M.G., Murthy, M.R.L.N., Begum, R.J. and Satya Murthy, N.S., Phys. Stat. Sol., (a) 3 (1970) 959

Pd$_2$MnIn is the first and only one antiferromagnetic Heusler alloy to be observed.[10,18]. The magnetic structure is similar to that for MnO. The magnetic lattice consists of parallel (111) planes in which all the manganese atoms are coupled ferromagnetically. Neighbouring (111) planes are coupled antiferromagnetically.

A summary of the magnetic and structural properties of Heusler alloys is given in table 1.

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(18) Webster, P.J. and Tebble, R.S., Phil. Mag., 16 (1967) 347-60