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STUDIES ON THE HEUSLER ALLOYS–III. THE ANTIFERRO-MAGNETIC PHASE IN THE Cu-Mn-Sb SYSTEM

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Abstract—A micrographic study of some alloys of the Cu-Mn-Sb system in both the as-cast and heat-treated conditions, revealed the presence of a single phase alloy (lattice parameter, $a = 6{\cdot}088 \pm 0{\cdot}003$ Å) at the composition CuMnSb. Alloys having slightly less copper than the stoichiometric alloy also consisted of a single phase, although quenching was usually necessary to prevent the appearance of a second phase. Alloys with higher copper concentrations, including the alloy of composition Cu_2MnSb, contained an α-Cu solid solution, as well as the intermediate phase. X-ray and neutron diffraction investigations of CuMnSb showed the alloy to have an ordered MgAgAs (Cl_b) type structure with Cu atoms at 0, 0, 0; Mn atoms at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; and Sb Atoms at $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$. Antiferromagnetic reflections appeared in neutron diffraction scans at 4·2°K and were indexed using a magnetic unit cell with twice the edge lengths of the chemical unit cell. The magnetic moments of the manganese atoms were found to be oriented perpendicular to the ferromagnetic (111) planes and parallel to the [111] direction of the rhombohedral magnetic cell. The average magnetic moment per manganese site was determined to be $3{\cdot}9 \pm 0{\cdot}1\ \mu_B$.

1. INTRODUCTION

EXPERIMENTS by earlier workers indicated the existence of ternary phases in the Cu-Mn-Sb system. Heusler *et al.*[1] reported the existence of a single phase alloy at the composition Cu_2MnSb, which was ferromagnetic, and exhibited the Heusler structure. Valentiner and Becker[2] studied the magnetic properties of this alloy and confirmed its ferromagnetic nature. More recently, however, investigations by Oxley *et al.*[3, 4] seemed to indicate that Cu_2MnSb was paramagnetic at room temperature but was antiferromagnetic below 38°K. They attributed earlier results to be due to the presence of ferromagnetic MnSb in the alloy. These conflicting results prompted the present study which is part III of a general study of the atomic and magnetic structures of the Heusler alloys. A detailed description of the Heusler structure was given in Part I of this series[5].

Apart from the alloy Cu_2MnSb, one other ternary phase has been reported. Castelliz[6] found a single phase alloy at the composition CuMnSb which has a crystal structure very similar to that of the Heusler alloys. Nowotny and Glatzl[7] used X-ray diffraction photographs to determine that the atomic arrangement was of the MgAgAs(Cl_b) type and the same as the Heusler structure except that one of the four partial lattices, (that consisting of the *C* sites) was vacant. By filling this partial lattice with copper atoms one might expect to arrive at the Heusler alloy of composition Cu_2MnSb.

No micrographic studies were mentioned in the literature and the assumption of a homogeneous single phase alloy was usually based on an X-ray powder photograph which reveals no other reflections than those attributable to the ordered Heusler-type phase. One of the aims of this investigation was to examine the microstructures of various alloys in the Cu-Mn-Sb system.

2. APPARATUS AND MATERIALS

The alloys were prepared by melting together weighed quantities of the constituent metals (each of high purity), using a high frequency induction furnace. Argon was used as a protective atmosphere and the melt was contained in recrystallised alumina crucibles. Loss of components during melting was usually less then 0·3 per cent. Heat treatment procedures were carried out with the samples sealed in evacuated silica capsules.

The X-ray diffraction patterns were obtained with a horizontal diffractometer mounted on a Philips 1010 X-ray unit using nickel filtered copper radiation. Provision was made for rotation of the powdered sample, and the intensities of the reflections were measured by point counting for fixed time intervals (usually 30 sec) with steps of 1 min of arc, 2θ.

The neutron diffraction experiments were carried out on the Australian Institute of Nuclear Science and Engineering powder diffractometer at Lucas Heights. The neutron beam from the reactor, HIFAR, had a wave length of 1·07 Å after reflection from a copper single crystal monochromator. The powdered specimen was contained in a vanadium can for runs at room temperature. The boron trifluoride detector was moved in three minutes of arc 2θ steps.

3. RESULTS

Microstructure

From microscopic examination of as-cast, annealed and also quenched alloys of the Cu-Mn-Sb system the only single phase alloys found (apart from dilute solutions) had compositions very close to CuMnSb. As the copper content was decreased a second phase began to appear in the slowly cooled alloy at about the composition $Cu_{0\cdot85}MnSb$, while samples quenched from just below the melting point revealed the precipitation of a second phase at the composition $Cu_{0\cdot75}MnSb$. A second phase (α-Cu solid solution) also appeared as soon as the copper concentration was increased above the 1:1:1 ratio. This confirmed the results of Castelliz[6] who found that, in contrast to the Ni-Mn-Sb system, the homogeneity region of the ordered cubic phase does not extend much beyond the stoichiometric composition CuMnSb.

Microscopic examination of the polished and etched section of the alloy Cu_2MnSb in the slowly cooled condition revealed about 60 per cent primary grains in a eutectic-type matrix (see Fig. 1). An X-ray diffraction photograph revealed the presence of an α-Cu solid solution with lattice parameter, $a =$ 3·66 Å. Variations in the heat treatment of the alloy failed to produce a single phase structure. Electron probe micro-analysis established that the primary phase had a compostion very close to CuMnSb.

Structure of CuMnSb

The X-ray diffraction pattern obtained from a well annealed sample of CuMnSb is shown in Fig. 2. It can be seen that the alloy is face centered cubic and the lattice parameter, a, was determined to be 6·088 ± 0·003 Å. This compares with 6·071 Å obtained by Castelliz[6] and 6·066 Å obtained by Nowotny and Glatzl[7]. Oxley *et al.*[3] obtained a lattice parameter of 6·097 ± 0·004 Å for the alloy Cu_2MnSb.

Density measurements indicated that there were very close to twelve atoms per unit cell and for an ordered alloy the space group would be $F\bar{4}3m$. Of the four partial lattices available it might be expected that only three of these would be filled in this particular case. The possible ordered distributions of the three types of atoms over the four partial lattices are shown in Table 1.

The equations for the structure amplitude, $|F_{hkl}|$, for an alloy consisting of four interpenetrating f.c.c. lattices have been given in Paper I of this series[5]. Since the reflec-

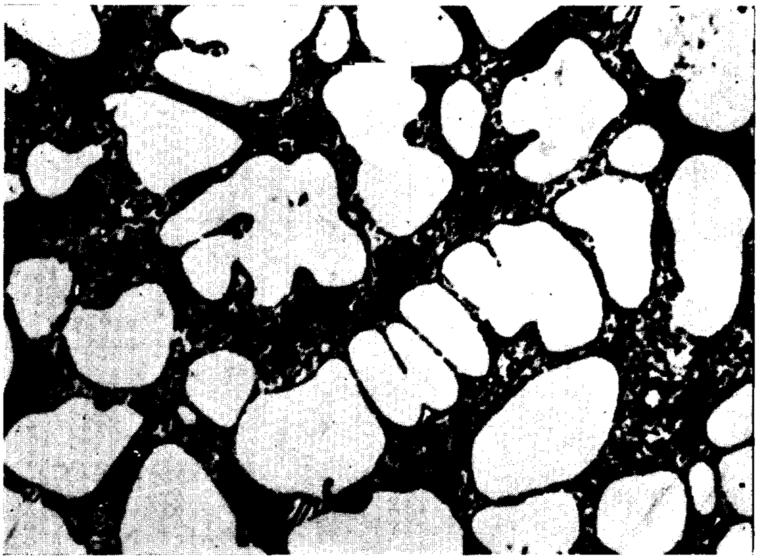

Fig. 1. Microstructure of Cu_2MnSb (slowly cooled) showing primary grains of CuMnSb. Etched in NH_4OH; H_2O_2 solution. Magnification ×500.

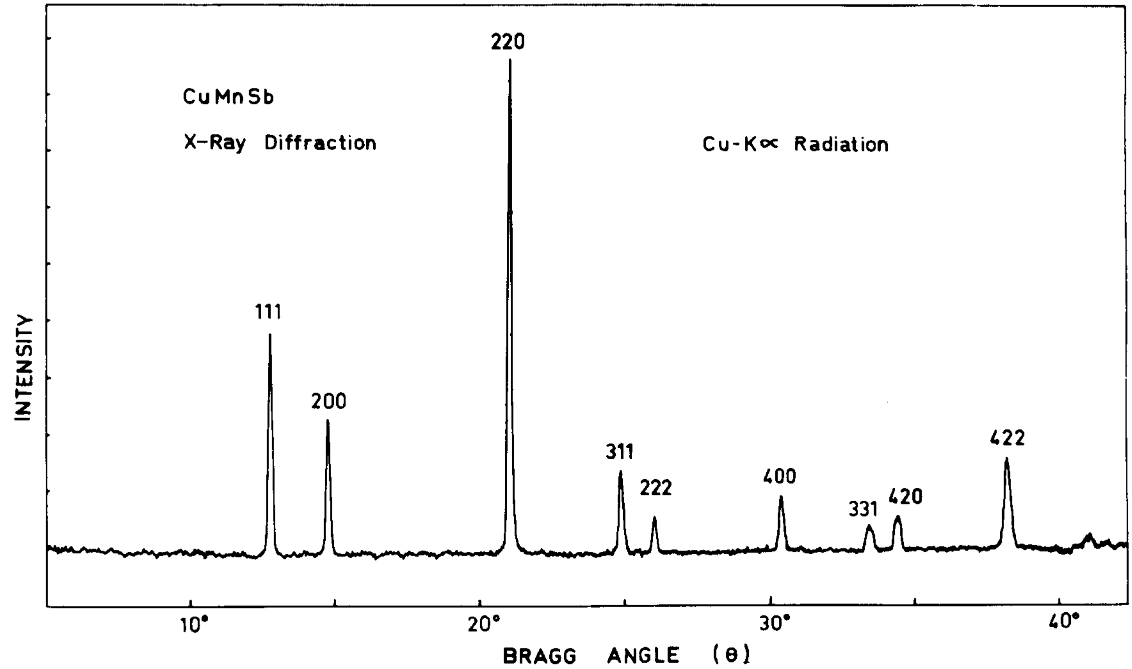

Fig. 2. X-ray diffraction trace of CuMnSb using nickel-filtered copper radiation.

Table 1. *Possibilities of an ordered distribution of the atoms of* CuMnSb *over the four partial lattices*

Designation of filling Possibilities	*A* 0, 0, 0 + F. C. T.*	*B* $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ + F. C. T.*	*C* $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ + F. C. T.*	*D* $\frac{3}{4},\frac{3}{4},\frac{3}{4}$ + F. C. T.*
I	Cu	Mn		Sb
II	Cu		Mn	Sb
III	Cu	Mn	Sb	

*Face-centering Translations

tions can be divided into three groups it is only necessary to calculate the structure amplitudes for a set, such as 111, 200, and 220. The square of the structure amplitudes calculated for the various atomic distributions are compared with the observed values in Table 2.

The results favour the atomic distribution I. This is in agreement with the results of Nowotny and Glatzl[7] who had greater difficulty because they estimated the intensities from a powder photograph. However, because the atomic scattering powers of copper and manganese for X-rays are very similar, any partial disorder among these atoms would be difficult to detect from X-ray diffraction data alone, and so neutron diffraction experiments were carried out and yielded the diffraction pattern shown in Fig. 3.

The observed neutron diffraction structure factors together with the calculated structure

Table 2. *X-Ray diffraction results*

Reflection *h k l*	Observed $|F_{hkl}|^2$	Calculated $|F_{hkl}|^2$ for various atom distributions I	II	III
1 1 1	0·183	0·189	0·313	0·125
2 0 0	0·239	0·228	0·001	0·352
2 2 0	1·000	1·000	1·000	1·000

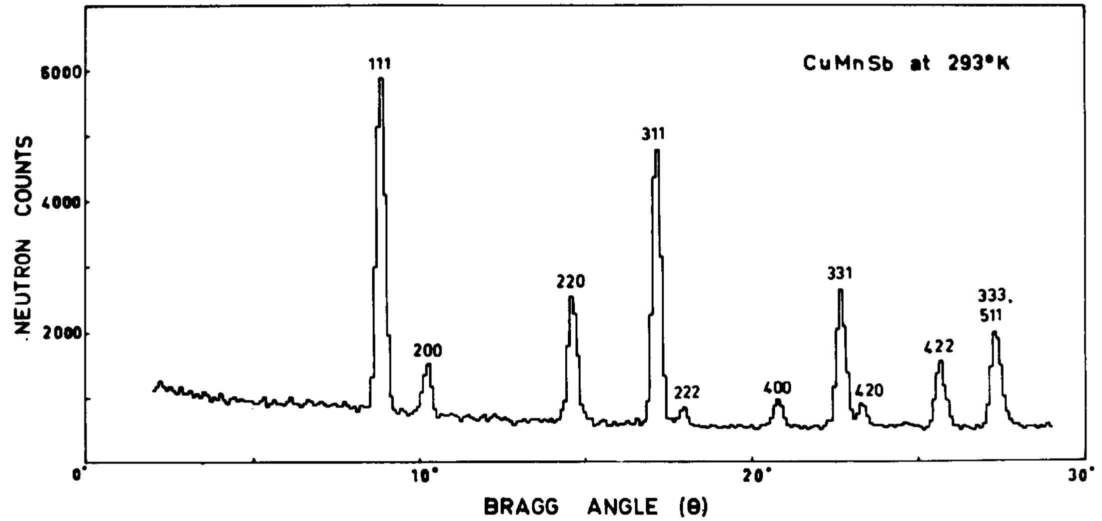

Fig. 3. Neutron diffraction histogram of CuMnSb at room temperature.

factors are given in Table 3. It is apparent that the best correlation between observed and calculated structure amplitudes is again obtained with the atom distribution I. However the observed values are slightly lower than the calculated values and this suggests that a very small amount of disorder may be present in the alloy. The best agreement between calculated and observed structure factors is obtained if it is assumed that 0·5 per cent of the copper atoms occupy *B* sites while a corresponding number of manganese atoms occupy *A* sites. It should be pointed out, however, that this small degree of partial disorder may not really exist because the discrepancies in the structure amplitude ratios are almost small enough to be attributed to experimental error. The neutron diffraction measurements have confirmed the results of X-ray diffraction, i.e. that CuMnSb is essentially fully ordered.

Although CuMnSb is paramagnetic at room temperature and is not attracted by a magnet at the temperature of liquid nitrogen, the work of Castelliz[6] and of Oxley *et al.*[3] suggested that it may be antiferromagnetic at very low temperatures (possibly at temperatures below 38°K). A neutron diffraction study using a liquid helium cryostat therefore seemed worthwhile.

The Magnetic Structure of CuMnSb

The neutron diffraction pattern of CuMnSb obtained at liquid helium temperature is shown in Fig. 4. It contains not only the coherent nuclear scattering peaks similar to those obtained at room temperature, but also a number of extra peaks corresponding to the

Table 3. *Room temperature neutron diffraction results for* CuMnSb

Reflection *h k l*	Observed $/F_{hkl}/^2$	Calculated $/F_{hkl}/^2$ for various atom distributions		
		I	II	III
1 1 1	1·50	1·524	1·705	0·205
2 0 0	0·38	0·395	0·013	3·040
2 2 0	1·00	1·000	1·000	1·000

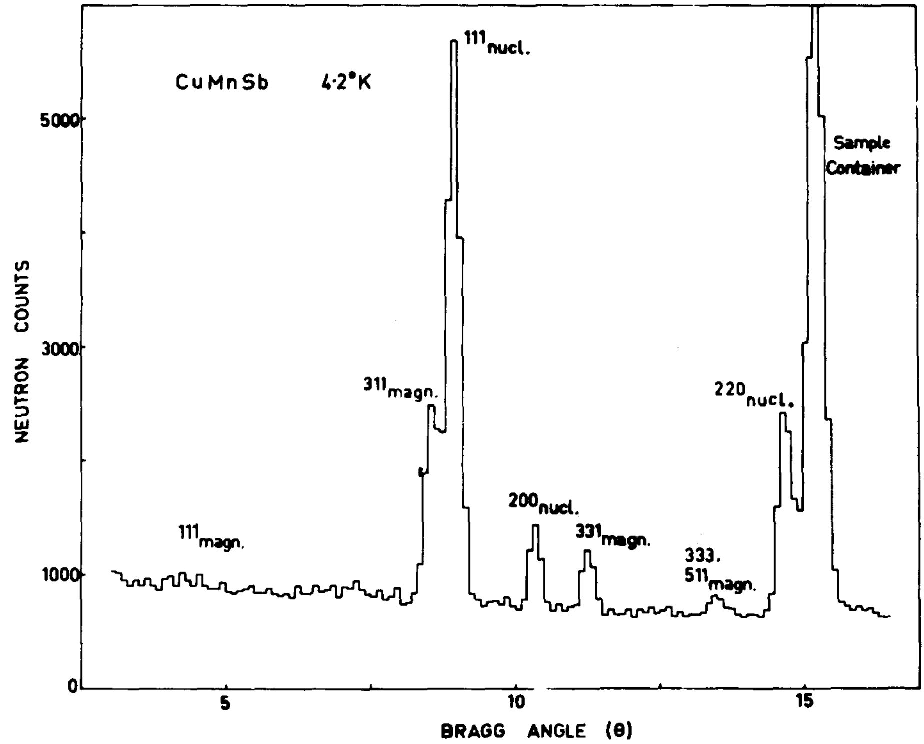

Fig. 4. Neutron diffraction histogram of CuMnSb at 4·2°K showing the reflections from the antiferromagnetic manganese sublattice. Note the absence of the 111 magnetic reflection.

magnetic scattering. These additional peaks can be indexed in terms of a magnetic unit cell with lattice parameter twice that of the chemical unit cell. The additional lines are all odd and correspond to the 311, 331, 511, etc. reflections from the enlarged unit cell. If it is assumed that the entire magnetic moment resides on the manganese atoms, then the enlarged magnetic unit cell indicates that successive manganese atoms along the cube axes are oriented differently.

These results suggest that the magnetic structure is rather similar to that of MnO which has rhombohedral symmetry below the Néel temperature. The magnetic structure of MnO was first determined by Shull *et al.*[8] and has been modified slightly by later workers (see, for example, Roth[9]). The magnetic lattice consists of parallel (111) sheets within which all the manganese atoms are coupled ferromagnetically. Alternate (111) sheets are coupled antiferromagnetically.

From measurements of the nuclear scattering intensities at liquid helium temperature it was deduced that the alloy was fully ordered because the structure amplitudes were almost identical to those calculated for distribution I in Table 3. Since the manganese atoms appear to occupy the *B* sites exclusively at 4·2°K it may be assumed that the whole of the magnetic moment resides on this type of site.

There are three cases of interest concerning the relative orientations of the magnetic moments and the lattice axes:

(i) The magnetic moments are aligned along the cube axes, i.e. along arbitrary [100] directions.

(ii) The magnetic moments are oriented perpendicular to the ferromagnetic (111) sheets in the [111] direction.

(iii) The magnetic moments are aligned arbitrarily in the ferromagnetic (111) sheets.

Shirane[10] has pointed out that with powder samples a unique solution to the problem of the spin orientation is only obtained in case (ii) where $q^2 = 0$ for the 111 reflection. q^2 is equal to $\sin^2 \alpha$ where α is the angle between the magnetic and scattering vectors.

Table 4 summarises the calculated magnetic structure amplitudes for each of these three cases for comparison with the experimentally observed structure amplitudes. The calculated values were obtained assuming that the moment on the manganese atom was $4\mu_B$ per atom. This is considered to be due to spin only as the orbital contribution is assumed to be quenched by the crystal field. Also the calculated values are normalised against the 311 measured reflection, which is itself normalised against the 220 reflection.

Since the observed intensity of the 111 magnetic reflection was zero it is obvious that we have the situation given in case (ii). Thus, assuming there is only a single magnetic axis (i.e. the [111] direction), the magnetic moments are all aligned parallel to this direction and the direction of magnetisation is reversed on adjacent planes. The alignment of the spins on the manganese atoms is shown in Fig. 5.

The neutron diffraction measurements indicate that the average magnetic moment per manganese site at the temperature of liquid helium is $3{\cdot}9 \pm 0{\cdot}1\ \mu_B$, assuming that the moment is due entirely to electron spin.

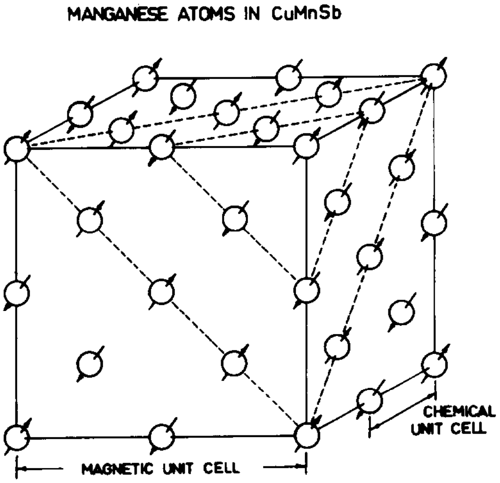

Fig. 5. The antiferromagnetic alignment of the spins of the manganese atoms in the [111] direction in CuMnSb at 4·2°K.

4. DISCUSSION

In analysing the low temperature neutron diffraction results for CuMnSb it has been assumed that only manganese is the moment carrier. This assumption is usually made in studies of the Heusler alloys, especially those containing copper, and the results of work by Felcher *et al.*[11] on the magnetic moment distribution in Cu_2MnAl support this assumption. In such cases it is sometimes considered that the distance between the manganese atoms is important in controlling the magnetic properties.

Hames[12] has noted that the Mn-Mn

Table 4. Neutron diffraction data from CuMnSb *at liquid helium temperature*

h k l	$q^2/F/^2$ observed	q^2 [100]	$q^2/F/^2$calc. [100]	q^2 [111]	$q^2/F/^2$calc. [111]	q^2 [110]	$q^2/F/^2$ calc. [110]
1 1 1	0	2/3	0·969	0	0	1	1·875
3 1 1	0·710	2/3	0·710	32/33	0·710	17/33	0·710
3 3 1	0·318	2/3	0·525	32/57	0·306	41/57	0·734
5 1 1		2/3		32/81		65/81	
3 3 3	0·14	2/3	0·326	0	0·157	1	0·602

distances in the strongly ferromagnetic Heusler-type alloys range from 4·08 Å for Co_2MnGa to 4·42 Å for PdMnSb. In Pd_2MnSb, which is weakly ferromagnetic, the distance is 4·55 Å. The Mn–Mn distance for CuMnSb is 4·30 Å, which lies in the middle of the range and it therefore appears that nearest neighbour manganese interactions may play a relatively unimportant role in determining the spin alignment. This is also suggested by the fact that both ferromagnetic and antiferromagnetic alignment exist between nearest neighbour manganese atoms, while next nearest neighbour manganese atoms are always antiferromagnetically aligned. However, it seems pointless to attempt an explanation of the antiferromagnetism of CuMnSb especially when one considers the inadequacy of present theories to explain the magnetic properties and structures of the Heusler alloys.

The magnetic moment for CuMnSb of 3·9 μ_B at 4·2°K obtained in this work may be compared with the saturation magnetisations of those Heusler alloys containing copper. These have been measured by many investigators, usually with slightly different results, but they indicate that the average manganese moment is approximately 4·0 μ_B per atom at temperatures approaching 0°K.

5. CONCLUSION

The conflicting reports in the literature concerning the alloy Cu_2MnSb probably resulted mainly from the fact that this alloy does not consist of a single phase. It consists of the alloy CuMnSb and an α-Cu solid solution. Powder X-ray and neutron diffraction data confirmed that CuMnSb has the MgAgAs($C1_b$) structure. Powder neutron diffraction data at 4·2°K were sufficient to determine that the manganese moments in successive (111) planes were antiferromagnetically aligned with each moment parallel to the [111] direction, yielding a magnetic unit cell with edge lengths twice that of the chemical unit cell and having rhombohedral symmetry.

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