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Observations on the Ferromagnetic β Phase of the Cu–Mn–Sn System

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The copper-rich portion of the copper–manganese–tin system was investigated by X-ray diffraction, electron microprobe, and magnetometric techniques. A model for the ordering taking place in the β phase was established. Two low-temperature phases for the alloy composition Cu_2MnSn were identified, and the existence of the intermetallic compound Cu_4MnSn was confirmed. Another low-temperature phase was found; it is α or β manganese, and its appearance contradicts previous investigations. The saturation magnetizations were measured and correlated with a function of the long-range ordering in the β structure.

Introduction

In 1898 Friederich Heusler discovered that certain Cu–Mn–Sn and Cu–Mn–Al alloys were ferromagnetic. Since then a number of investigators have explored the structural and magnetic properties of these alloys and found ferromagnetism to be associated with a β phase. This solid solution is ordered and stable at temperatures greater than 400 °C and can be retained at room-temperature through quenching. The highest magnetization in the Cu–Mn–Sn alloys ($M_s = 660$ emu cm^{-3}) is encountered at the composition Cu_2MnSn (Carapella & Hultgren, 1942). The ordered β phase consists of a body-centered structure with a face-centered superlattice. A model of the ordered structure has been proposed but has remained untested (Persson, 1929; Carapella & Hultgren, 1942; Webster, 1969). An investigation of a series of alloys by Valentiner (1953) detected a low-temperature intermetallic compound tentatively identified as Cu_8Mn_4Sn or Cu_4MnSn; the latter compound was later confirmed by Gladyshevskii *et al.* (1961). Taglang & Asch (1954) found ε-Cu_3Sn to be one of the phases resulting from the low-temperature decomposition of Cu_2MnSn.

Ordering

A model for the ordering taking place in the β phase was established as shown in the following discussion. Fig. 1 shows the β phase of the Cu–Mn–Sn system, a body-centered structure with a face-centered superlattice. Atomic sites were divided into four types and designated by *A*, *B*, *C*, and *D*. Ordering was detected and identified through X-ray distribution analysis which has been previously described (Bradley & Rogers, 1934; Heusler, 1934). Three ordering models were assumed, and the positions of Cu, Mn, and Sn, referred to the four types of sites shown in Fig. 1, are shown in Table 1.

Table 1. *Theoretical ordering models*

	Atomic site			
Model	*A*	*B*	*C*	*D*
1	Cu	Mn	Cu	Sn
2	Cu or Mn	Cu or Mn	Cu or Mn	Sn
3	Mn	Cu	Cu	Sn

Copper and manganese have very close atomic numbers. Their X-ray scattering factors are therefore nearly identical, and ordering among these atoms is difficult to detect. This problem is overcome, however, by taking advantage of anomalous dispersion near the *K* absorption edge of Cu and Mn. Of the targets available, Fe $K\alpha$ and Cu $K\alpha$ radiation were found to give the best discrimination. The atomic scattering factor of Mn atoms for Fe $K\alpha$ radiation is significantly lower than normal because of anomalous dispersion, while that of Cu retains its normal value for this radiation. Inversely, the atomic scattering factor of Cu atoms for Cu $K\alpha$ radiation is abnormally low, while that for Fe retains its normal value. These differences allow for discrimination of crystalline planes containing mostly Cu from those containing mostly Mn. The dispersion corrections used in the present investigation were taken from Bradley & Rodgers (1934) and *International Tables for X-Ray Crystallography* (1962).

An alloy of composition Cu_2MnSn was prepared by induction melting under an argon atmosphere and homogenized for 300 hours at 350 °C. By microprobe analysis of prior melts, such an annealing treatment had been shown to be adequate for homogenizing. After being slowly cooled to room temperature, it was reduced to powder, encapsulated in a vycor tube under argon atmosphere, and heated to 600 °C for 3 hr. The alloy was then quenched in brine, the vycor capsule being broken by a glass hammer, and X-ray diffraction analysis was performed on the powder. The integrated intensities observed with a diffractometer are compared in Tables 2 and 3 with values computed for mo-

dels 1, 2, and 3; computations included Lorentz–polarization, multiplicity, temperature ($B=0{\cdot}3$) and structure factors (*International Tables for X-Ray Crystallography*, 1962).

Table 2. *Observed and calculated intensities of lines for* Cu *Kα*

	Calculated			
Line	Model 1	Model 2	Model 3	Observed
111	130	115	108	110±14
200	45	60	67	45±24
220	1,000	1,000	1,000	1,000
311	55	51	49	62±15
222	12	47	16	17±1
400	133	133	133	143±4
331	24	42	22	26±6
420	14	17	18	32±2
422	222	222	222	245±5
511–333	13	13	12	–
440	63	63	63	76±8

Table 3. *Observed and calculated intensities of lines for* Fe *Kα*

	Calculated			
Line	Model 1	Model 2	Model 3	Observed
111	200	136	132	190±22
200	34	76	103	47±5
220	1,000	1,000	1,000	1,000
311	85	62	96	84±27
222	7	18	24	11±20
400	135	135	135	125±56
331	29	25	22	17±17
420	10	23	33	–
422	292	292	292	257±32

Three types of reflection are present:

$\sum h=4n$: 220, 400, 422 ... fundamental lines
$\sum h=4n-2$: 200, 222, 420 ... superlattice lines
$\sum h=2n+1$: 111, 311, 331 ... superlattice lines .

A comparison of various significant ratios of intensities in Tables 2 and 3 leads to the conclusion that ordering takes place mainly according to model number 1, the $L2_1$ structure (Persson, 1929; Carapella & Hultgren, 1942; Webster, 1969). Prior assumptions of this type of ordering are thus confirmed by the present intensity measurements and their critical comparison (for the first time) with all three models.

In addition to the alloy Cu_2MnSn, a series of alloys in the β-phase range were prepared and quenched. The alloys are designated by numbers 1 through 5, and their compositions are schematically shown in Fig. 2. Superlattice lines, indicative of long-range ordering, were found in all these alloys, in conformity with previous conclusions (Carapella & Hultgren, 1942) that long-range ordering exists over a wide portion of the β-phase range.

Room-temperature phases

X-ray analysis showed that the high-temperature β phase was not fully retained, so a study was carried on to identify the room-temperature phases that might be present. Debye–Scherrer photographs showed that the lattice parameters of the β phase varied according to the prepared compositions in at. % as shown in Table 4.

Table 4. *Lattice parameters of the β phase*

No.	Alloy composition in at. %			Lattice parameter in Å
	Cu	Mn	Sn	
1	64·8	26·5	8·7	6·084±0·008
2	57·6	32·3	10·1	6·066±0·003
3	55·3	29·6	15·1	6·125±0·001
4	52·7	27·1	20·2	6·151±0·015
5	50·1	24·8	25·1	6·176±0·009

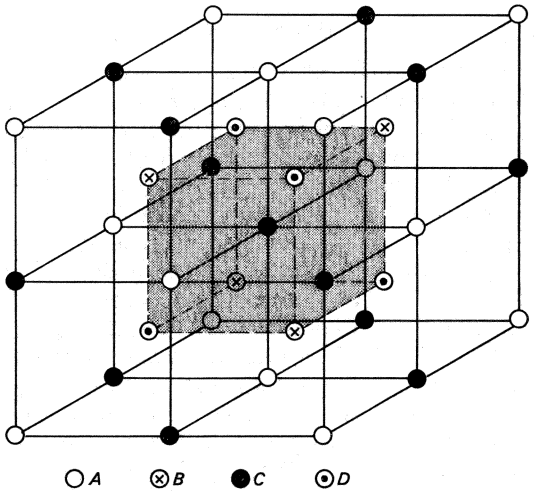

Fig. 1. The β phase of the Cu–Mn–Sn system.

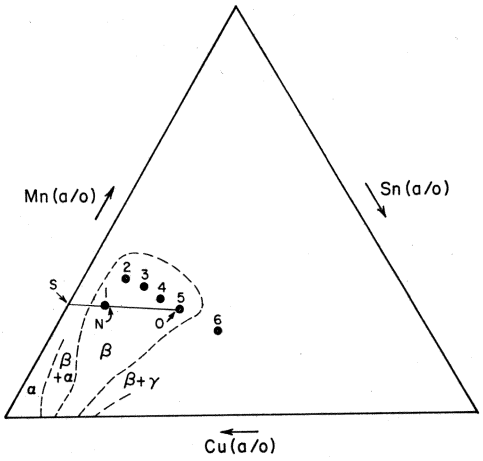

Fig. 2. Maximum β-phase range and composition of alloys ($T\sim600$ °C).

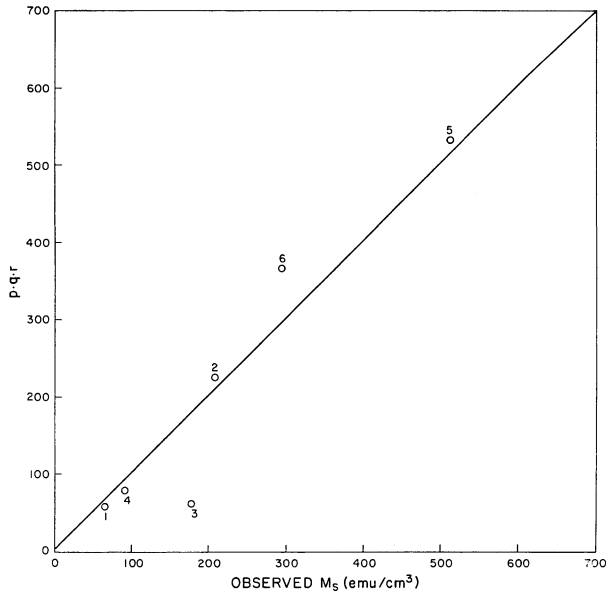

Fig. 3. Observed *vs.* calculated saturation magnetizations.

A low temperature Cu_4MnSn type structure with a constant lattice parameter of $6{\cdot}982 \pm 0{\cdot}003$ Å was also present in all the alloys; this compares with $6{\cdot}988 \pm 0{\cdot}003$ as reported by Gladyshevskii *et al.* (1961). These observations lead to the conclusions that the composition of the β phase is the same as the prepared composition of the alloy, while the room-temperature structure is that of an intermetallic compound. Electron probe microanalysis established the composition of Cu_4MnSn for the compound within an accuracy limit of ± 4 at. %, confirming previous communications (Valentiner, 1953; Gladyshevskii *et al.*, 1961). Furthermore, it showed the presence of a phase consisting of nearly pure manganese with small amounts of copper (0·40–2·29 at. %) and tin (0·09–0·41 at. %) in solid solution. (With Debye–Scherrer photographs it was not possible to ascertain whether it was α or β manganese.) A third room-temperature phase was also present as a fine precipitate, but it could not be identified. No ε-Cu_3Sn was identified, in contradiction to the results of Persson (1929) and Taglang & Asch (1954).

Structure and magnetism

Elucidation of a correlation between magnetism and structure would be desirable, but neither the present nor earlier data are sufficiently detailed to support tests of elaborate models. One of the simplest was therefore chosen. An ordering function p was arbitrarily chosen, varying linearly from $p=1$ at Cu_2MnSn, to $p=0$ at the boundary of the diagram, along a straight line extending from Cu_2MnSn through each given alloy; thus in Fig. 2 for alloy number 1, plotted at the point N, $p=1-ON/OS$. It was also assumed that the saturation magnetization of an alloy in the β phase range is given by the product $p \times q \times r$, where q is the fraction of β phase retained (as judged by the intensity of its diffraction lines) and r is the highest value of saturation magnetization ever reported for a Cu_2MnSn alloy, namely 660 emu cm^{-3} (Carapella & Hultgren, 1942). Fig. 3 shows the correlation obtained between $p \times q \times r$ and the observed saturation magnetizations. The plotted line shows $p \times q \times r$ equal to M_s which should theoretically be the case. Alloy number 6 deserves less weight because the composition of the β phase is unknown; lacking further information, it is plotted assuming that its composition is the same as the overall composition of the alloy. There were indications that alloy number 3 was slightly oxidized, which might explain its low value on the plot. The model indicates that these assumptions lead to a rough approximation of the observed magnetizations for most alloys and that, consequently, structural measurements allow a reasonably good prediction of the saturation magnetizations, in spite of the simplifications used.

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