

New Sigma-Phases in Binary Alloys of the Transition Elements of the First Long Period

THE structure of the brittle intermediate σ -phase in the system iron-chromium has not yet been determined; but isomorphous phases have been found in the systems iron-vanadium¹, cobalt-chromium² and iron-molybdenum³. All these phases occur at or near to the equiatomic composition, and this has led K. W. Andrews⁴ to suggest that they are connected with superlattice formation. Recent work in this Laboratory has led to the discovery of four new σ -phases the compositions of which are of interest. The existence of two of these phases was predicted by Beck and Manly⁵.

(1) *Chromium-manganese*. The intermediate phase in this system, previously denoted θ^2 , has a typical σ -phase structure, and its composition range extends from approximately 72 to 83 atomic per cent manganese.

(2) *Vanadium-manganese*. The equiatomic alloy has a body-centred cubic structure; but an alloy containing 24.3 atomic per cent vanadium gave a typical σ -phase powder pattern though the microstructure was not homogeneous.

(3) *Vanadium-cobalt*. An alloy containing 50.5 atomic per cent vanadium has a σ -phase structure. This is consistent with the results of Köster and Lang⁷ for the ternary system iron-cobalt-vanadium.

(4) *Vanadium-nickel*. An alloy containing 55 atomic per cent vanadium has the σ -phase structure; and this phase extends from about 55 to more than 65 atomic per cent of vanadium, and is probably stable up to the solidus.

The interplanar spacings for the vanadium σ -phases are slightly greater than those for the chromium σ -phases, as would be expected from the known atomic diameters. It is found that a single multiplication factor enables all the interplanar spacings of any one σ -phase to be converted into those of another. The multiplication factors necessary to make the observed d -values equal to those for the chromium-manganese phase are shown in the accompanying table, and the agreement is exact within the limits of experimental error.

System	Cr-Mn	Cr-Fe	Cr-Co	V-Mn	V-Fe	V-Co	V-Ni
Composition of the alloy	Mn 75.5% Cr 24.5%	—	—	Mn 75.7% V 24.3%	Fe 52% V 48%	Co 49.5% V 50.5%	Ni 45% V 55%
Multiplication factor	1	1.002	1.012	0.9935	0.9908	0.9984	0.9930

The above results show that the formation of σ -phases is not connected with an equiatomic superlattice, and support the suggestion of Sully and Heal⁸ that σ -phases are electron compounds. We have not been able to obtain a σ -phase in vanadium-chromium alloys, and the present results therefore suggest that, in binary alloys of the First Long Period, σ -phases are found only in alloys of vanadium with elements from manganese to nickel, and in alloys of chromium with elements from manganese to cobalt. Bradley and Goldschmidt⁹ state that the σ -phase structure corresponds to a distorted body-centred cube, and it is interesting to note that the phase apparently always occurs in equilibrium with a solid solution in the body-centred cubic metals chromium and vanadium.

Note added in proof. Our attention has been directed to a recent paper by Pietrokowsky and Duwez¹⁰, who have also found σ -phases in vanadium-cobalt and vanadium-nickel alloys.

W. B. PEARSON
J. W. CHRISTIAN
W. HUME-ROTHERY

Inorganic Chemistry Laboratory,
Oxford.
Oct. 20.

¹ Wever, F., and Jellinghaus, W., *Mitt. K.W. Inst. Eisenforsch.*, **12**, 317 (1930).

² Wever, F., and Haschimoto, U., *Mitt. K.W. Inst. Eisenforsch.*, **12**, 353 (1930).

³ Goldschmidt, H. J., *Research*, **2**, 343 (1949).

⁴ Andrews, K. W., *Research*, **1**, 478 (1948).

⁵ Beck, P. A., and Manly, W. D., *Trans. Amer. Inst. Min. Met. Eng.*, **185**, 354 (1949).

⁶ Carlile, S. J., Christian, J. W., and Hume-Rothery, W., *J. Inst. Metals*, **76**, 169 (1949).

⁷ Köster, W., and Lang, K., *Z. Metallkunde*, **30**, 350 (1938).

⁸ Sully, A. H., and Heal, T., *Research*, **1**, 288 (1948).

⁹ Bradley, A. J., and Goldschmidt, H. J., *J. Iron and Steel Inst.*, **144**, 273 (1941).

¹⁰ Pietrokowsky, P., and Duwez, P., *Trans. Amer. Inst. Min. Met. Eng.*, **188**, 1283 (1950).

Formation of Order in the Alloy CdMg₃

THE formation of a superlattice in the alloy AuCu₃ has been found to be accompanied by interesting X-ray diffraction effects^{1,2}; superlattice lines on powder photographs gradually build up from the background, starting as very broad bands and sharpening gradually as perfect long-range order develops. This phenomenon has been shown, both theoretically³ and by optical analogy⁴, to be due to increase in the short-range order in the alloy.

So far, AuCu₃ seems to be the only alloy for which this phenomenon has been reported, with the possible exception of certain compositions in the copper-palladium system⁵. We have now found that similar effects occur for the alloy CdMg₃; this has a critical temperature of 160°C., and order develops fairly rapidly even at room temperature⁶.

Since CdMg₃ is hexagonal, its powder photograph is much more complicated than that of AuCu₃, and when order develops many of the superlattice lines, particularly those at high angles, cannot easily be measured. The low-angle superlattice lines appear to be rather broader than the main-lattice lines; but those at higher angles, which should establish the effect with more certainty, are not easily seen in the background of the main-lattice lines.

This difficulty has been overcome by the use of single crystals. A single crystal was made by slowly cooling a small piece of the alloy from the melt at about 500°C. At these temperatures magnesium is readily attacked by both silica and air, and it was found necessary to place the alloy in an iron container in a silica tube containing argon at a low pressure.

X-ray oscillation photographs showed that the crystal was accompanied by one or two small satellites, but the superlattice spots could be clearly seen; and they were found to be definitely broader than the main-lattice spots. They sharpened appreciably when the crystal was left for several days at room temperature.

We propose to examine the shapes of the spots and to follow the changes in these shapes as order