Structural and Magnetic Properties of the Fe_{3-x}Mn_xAl System

A. S. ILYUSHIN* AND W. E. WALLACE

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received September 18, 1975; in revised form, December 1, 1975

Structures, bulk magnetic properties and Mössbauer spectra for $Fe_{3-x}Mn_xAl$ ternaries have been determined. For samples quenched from 750°C the DO₃ structure is found for x = 0 to 0.75, the β -Mn structure from 1.25 to 3.00 and a two phase system between x = 0.75 and 1.25. The Curie temperature decreases as Fe in Fe₃Al is replaced by Mn, indicating a weakening of ferromagnetic exchange. The Mössbauer spectrum at room temperature for x = 0.75 is a singlet. The spectra in the ternaries having the β -Mn structure indicate two types of Fe. The intensities in the Mössbauer pattern suggest that Fe is preferentially occupying one of the sites in the β -Mn structure.

I. Introduction

The work of Köster and Wachtel (1) shows that Mn in the β -Mn structure can incorporate large amounts of Al in solid solutions, ~41 atomic percent. Alloys containing more than 5 atomic percent Al are stable in the β -Mn structure to room temperature; that is, they do not transform into the α -Mn structure. Köster and Wachtel find that when β -Mn is alloyed with Al it remains paramagnetic down to room temperature, but with a susceptibility which is increased by about 50% in the Alsaturated alloys over that of pure β -Mn. The alloy represented by the formula Mn₃Al is, of course, included in the composition range in which the β -Mn structure is stable and persists to room temperature. In this alloy Al is presumably distributed at random over the lattice sites; it is paramagnetic with a susceptibility, according to Köster and Wachtel, of 10.5×10^{-6} emu/g.

Fe₃Al occurs in the DO₃(BiF₃) structure. It is ferromagnetic with a Curie temperature of 750°K (2). There are two kinds of Fe in Fe₃Al-type I (4 per unit cell), in which all eight nearest neighbors are Fe and type II (8 per unit cell) for which half of the nearest neighbors are Al and half are Fe. Neutron diffraction work by Nathans et al. (3) showed many years ago that the iron moments are 2.1 and 1.5 μ_B per atom for type I and II Fe, respectively.

The present work forms part of a series of studies (4, 5) being carried out in this laboratory to study ternary systems containing Fe and Mn in an attempt to ascertain inter alia information in regard to the nature of the Fe-Mn exchange in such systems. In the present work we report on the structures and bulk magnetic properties of the Fe₃Al-Mn₃Al pseudobinary system.

Room temperature Mössbauer spectra were also obtained and are briefly mentioned.



FIG. 1. Lattice parameters for the $Fe_{3-x}Mn_xAl$ system. Fe₃Al and Mn₃Al exist in the DO₃ and β -Mn structures, respectively.

^{*} Visiting scholar from the Department of Physics, Moscow State University, USSR.

Copyright © 1976 by Academic Press, Inc.

All rights of reproduction in any form reserved. Printed in Great Britain



FIG. 2. Magnetization-temperature behavior of $Fe_{3-x}Mn_xAl$ alloys.

II. Experimental Procedure and Results

The ternary alloys were formed by fusing together the component metals in a water cooled copper boat under a stream of purified Ar. Induction heating was used. Purity of the metals was Fe and Mn, 99.9%; Al, 99.99%. These are purities exclusive of gaseous impurities.

The general experimental procedures followed those which are now standard in this laboratory. The recently published monograph by one of us (W.E.W) gives (6) numerous references to earlier work in this laboratory which contain descriptions of the techniques used.

The lattice parameters and the regions of stability of the DO₃ and β -Mn structures are shown in Fig. 1. These data are for materials which had been rapidly quenched to room temperature after heat treating for 100 hr at



FIG. 3. Mössbauer spectrum for $Fe_{2.25}Mn_{0.75}Al$ (DO₃ structure).

750°C. Magnetization-temperature results for several ternaries in the DO_3 structure are shown in Fig. 2.

Fe⁵⁷ Mössbauer spectra were obtained at room temperature for Fe₃Al and for the ternaries represented by the formula Fe_{3-x}Mn_xAl. The spectra for Fe₃Al indicated two six-line patterns in accordance with previous Mössbauer work (7) and the neutron diffraction studies referred to above. When the Mn content is that characterized by x = 0.25



FIG. 4. Mössbauer spectra for $Fe_{3-x}Mn_xAl$ alloys possessing the β -Mn structure.

and larger, the spectra become uninterpretable, undoubtedly because the Fe is randomly distributed over the lattice sites and is experiencing a range of hyperfine fields. It is clear, however, from the width of the Mössbauer absorption spectra that the Fe hyperfine field is reduced as the Mn content increases. Near the boundary of the Fe₃Al primary phase the spectrum consists of a single line (Fig. 3).

The Curie temperature of Fe₃Al is 470°C (2). It is clear from the results in Fig. 2 that replacement of Fe by Mn reduces T_c . This indicates that ferromagnetic exchange is weaker in the ternary system Fe_{3-x}Mn_xAl than in Fe₃Al. In this respect the present results indicate a consistent pattern in ternary systems containing Fe and Mn. Introduction of Mn in replacement of Fe leads to a decline in Curie temperature for a number of ternary systems which have been studied in this and other laboratories: Y₆F₂₃-Y₆Mn₂₃ (4), RFe₂-RMn₂ (5) (R is a rare earth element), Fe₃Ge-Mn₃Ge (8) and Fe₃Sn-Mn₃Sn (9).

Mössbauer spectra for ternaries in the β -Mn structure shown in Fig. 4 indicate that Fe is situated in at least two distinguishable sites. This is as expected since in β -Mn there are two crystallographically distinguishable sites. These sites are present in β -Mn in the ratio

12:8. If Fe were populating these two types of sites in a random fashion, we would expect two lines in the Mössbauer spectra with intensities in the ratio of 12 to 8. Clearly this is not the case (Fig. 4). From the observed spectra it appears that there is preferential site occupancy, which is rather surprising in view of the chemical similarity of Mn and Fe.

References

- 1. W. KÖSTER AND E. WACHTEL, Z. Metallk. 51, 271 (1960).
- For a summary of the magnetic properties of 3d transition metal intermetallics see: W. E. WALLACE, "Progress in Solid State Chemistry" (H. Reiss and J. O. McCaldin, Eds.), Vol. 6, p. 155 (1971)
- 3. R. NATHANS, M. T. PIGOTT, AND C. G. SHULL, J. Phys. Chem. Solids 6, 38 (1958).
- C. A. BECHMAN, K. S. V. L. NARASIMHAN, W. E. WALLACE, R. S. CRAIG, AND R. A. BUTERA, J. Phys. Chem. Solids, 37, 247 (1976).
- 5. A. S. ILYUSHIN AND W. E. WALLACE, J. Solid State Chem., 17, 373 (1976).
- 6. W. E. WALLACE, "Rare Earth Intermetallics," Academic Press, New York (1973).
- See, for example: K. ONO, Y. ISHIKAWA, A. ITO, AND E. HIRIHARA, J. Phys. Soc. Japan 17, Suppl. B-1, 125 (1962).
- Y. LECOCQ, P. LECOCQ, AND A. MICHEL, Compt. Rend. 256, 493 (1963).
- 9. J. S. KOUVEL, J. Appl. Phys. 36, 980 (1965).