The equilibrium ordered states for 400°C and 500°C annealing in Ni-Mn alloys near the Ni$_3$Mn composition have been investigated. The results indicate distinctly different order configurations for the two temperatures. At 400°C, homogeneous long range order results, with a saturation magnetization which is relatively insensitive to composition. At 500°C, the data suggest that the ordering is inhomogeneous, with the nucleation and growth of stoichiometric Ni$_3$Mn clusters in a Mn- or Ni-rich matrix, depending on composition.

### Introduction

One distinctive property of Ni-Mn alloys near the Ni$_3$Mn composition is, as first discovered by Kaya and Kussmann, that strong ferromagnetism appears with the development of Cu$_3$Au-type atomic order. In the perfectly ordered state, there are no antiferromagnetic Mn-Mn pairs and simple ferromagnetism results from the ferromagnetic Mn-Ni and Ni-Ni interactions. Previous work indicates that the magnetic state depends on, among other things, the annealing temperature. Based on magnetization data for a 22.7 at.% Mn alloy, Marcinkowski and Brown proposed that short range order results from ordering at temperatures above 480°C and homogeneous long range order results from ordering below 400°C. More recent data, however, suggest that the order is inhomogeneous above 480°C. The nickel-manganese phase diagram proposed by Tsipula-kis and Kneller shows the existence of many intermetallic compounds and two-phase regions. Domain observations by Lorentz microscopy and hysteresis measurements by Yokoyama and Satoh indicate that Mn content above 25 at.% and high annealing temperatures can result in inhomogeneous magnetic order.

With this background, the present study was undertaken in an attempt to clarify the nature of the equilibrium magnetic order state in Ni$_3$Mn alloys. Magnetization data were obtained for a range of compositions from 22.1 to 32.1 at.% Mn for two annealing temperatures, 400°C and 500°C. Measurements were made at low fields (0-8 kOe) from 4K to room temperature. Additional data in fields up to 100 kOe were obtained at 300K. Neutron diffraction data were also obtained. The results indicate distinctly different equilibrium order configurations for 400°C and 500°C annealing. The lower temperature annealing results in homogeneous long range ferromagnetic order as proposed by Marcinkowski and Brown. The high temperature annealing results in the development of stoichiometric, long range order domains.
The magnetization data shown in Figs. 1 and 2 are presented versus inverse static field in Figs. 3 and 4, respectively. This presentation is convenient, in that the high field values and the extrapolated saturation values can be easily compared. The solid lines represent the actual measurements and the dotted lines represent estimated extrapolations.

For 400°C annealing, the moment at 100 kOe exhibits the well-known maximum in the vicinity of 25 at.% Mn, which was explained by the existence of a superlattice structure and resultant ferromagnetic order. The extrapolated values suggest, however, that the saturation moment for 400°C equilibrium order is somewhat insensitive to composition. All curves, with the possible exception of the 32.1 at.% Mn sample, extrapolate to near 800 emu/cm³.

For 500°C annealing, both the high field data and the extrapolations indicate a maximum moment in the 24-29 at.% Mn range. The estimated saturation values are all substantially below the levels for 400°C annealing. Because the order is not saturated at the 50-hour annealing time used for these samples, these data may not be completely representative of the equilibrium state.

Neutron diffraction and x-ray data were also obtained. The 32.1 at.% Mn, 400°C sample was checked by powder x-ray diffraction for possible second phase content. Tsipiapakis and Kneller reported the existence of a Ni₂Mn phase near this composition. The present powder x-ray data did not show any evidence of a Ni₂Mn phase. Only the fcc Ni₃Mn phase was detected. While Laue diffraction does show evidence of subspots, divergent beam x-ray diffraction shows that these subspots originate from the mosaic structure of the alloy. The 24.6 and 26.2 at.% Mn samples, annealed at 500°C, were checked by neutron diffraction for superlattice development. The data were taken on rod samples which were annealed in the same manner as the spheres used in the magnetic studies. These two samples revealed well defined superlattice peaks.
The high field magnetization for 40°C annealing, as shown in Figs. 1 and 3, exhibits the well-known maximum in the vicinity of 25 at.% Mn. This is explained by the existence of a superlattice structure and resultant ferromagnetic order. The extrapolated saturation values, indicated in Fig. 3, are near 800 emu/cm³. This value is in good agreement with the theoretical value of 820 emu/cm³ for 25 at.% Mn, calculated by assuming that (1) all moments are parallel, (2) the Schottky and Wilkinson data on the atomic moments, $\mu_{\text{S}} = 3.2$ μ and $\mu_{\text{W}} = 0.3$ μ, are accurate, and (3) the lattice parameter is 3.89 Å. The maximum field of 100 kOe was insufficient to obtain precise extrapolated saturation moments. The data do suggest a shallow peak in saturation magnetization at 25 at.% Mn. Such behavior appears to be reasonable. For Mn above 25 at.% the excess Mn atoms tend to couple anti-ferromagnetically and the net moment decreases. For Mn below 25 at.% the relatively small moments of the Ni atoms also cause a reduction in the net moment.

The 40°C data show that the approach to saturation becomes harder for more Mn content. This indicates that the antiferromagnetic tendency, although overwhelmed by the ferromagnetic character, increases with Mn content. This result is consistent with both the Marcinkowski and Brown picture of homogeneous long range order at 400°C and the antiferromagnetic nature of Mn-Mn nearest neighbor interactions. As a result, the hardness to saturation (which may be taken as the slope of the magnetization versus inverse field curve at high field) will increase for Mn content above 25 at.% For Mn content below 25 at.% these considerations do not apply. The approach to saturation should be relatively easy and insensitive to small composition changes. Such expectations are confirmed by the data shown in Fig. 3. Previous Lorentz microscopy data also confirm the drastic effect of excess Mn on the magnetization in Ni-Mn alloys.

For 500°C annealing, the atoms are more mobile than at 400°C. The lower free energy for atomically ordered regions is likely to lead to an inhomogeneous order development in the form of ferromagnetic clusters of microscopic dimensions. Such a possibility was examined by Kneller. He estimated a cluster size on the order of 30 Å for 29.3 at.% Mn, annealed 20 hours at 480°C. A simplified cluster model was also used by Patton, et al., to qualitatively describe the order development at 500°C for a 26.2 at.% Mn alloy. These ordered clusters are likely to be those of the stoichiometric Ni₂Mn composition. Sato has suggested that, due to the magnetic contribution to the free energy, Mn atoms will tend to select Ni atoms as nearest neighbors, and that excess Mn atoms will be excluded from the Ni₂Mn order domain. These excess Mn atoms will tend to couple antiferromagnetically and will not contribute to the net moment. The tendency of the coercive force to increase with Mn content may be due to these excess Mn atoms between order domains. Since the overall magnetization is mostly due to ferromagnetic Ni₂Mn clusters, the magnetization curves are somewhat more rectangular than those for 400°C annealing. The existence of stoichiometric order domains at 500°C may also be inferred from the phase diagram of Ref. 3.

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References

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