Determination of the local structure of the first and second shells in ordered and disordered Ni-Mn alloys

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The coordination numbers and the interatomic distances for 50, 75 and 80 at.% Ni-Mn alloys in ordered and disordered states are presented. A new method for determining the first and second nearest neighbor coordination numbers in a binary alloy is applied. It is shown that magnetic properties of these alloys depend on short range order in atomic arrangement.

Keywords: EXAFS, structure of disordered alloys

1. Introduction

The $Ni_{0.75}Mn_{0.25}$ alloy forms an ordered phase of Cu_3Au type with suitable heat treatment. An increase in the degree of long range order in an alloy is often accompanied by extensive changes in magnetic and conductive properties of the alloy. A previous report (Okazaki, 1995) indicated that the increase of average magnetic moment in Ni_3Mn alloy with heat treatment depended on the degree of short-range order. The degree of short-range order for a Ni_3Mn alloy was estimated from long range order, evaluated by X-ray diffraction (XRD) studies.

An EXAFS study (Nakahata *et al*. (1997)) on Ni-Mn alloys revealed that the ratio between intensities of EXAFS signals of Ni and Mn K-edges depended on the arrangement of Ni and Mn atoms. However, there are serious problems in the determination of the structure parameters using the conventional approach (the least square method and Fourier filtering) for Ni-Mn alloys because of similar scattering characteristics of the atoms.

In this paper, we apply a new method of determining coordination numbers for ordered and disordered systems (Miyanaga, Okazaki, Babanov, *et al*., 1999) to study short range order in $Ni_{0.75}Mn_{0.25}$, in $Ni_{0.80}Mn_{0.20}$ alloys rapidly quenched or annealed under varied conditions to produce variations in the atomic arrangements and in a $Ni_{0.50}Mn_{0.50}$ alloy obtained by plastic deformation. Magnetic properties of these alloys depend on concentration and the structural state (Satoh, *et al*, 1978). For example, $Ni_{0.75}Mn_{0.25}$ alloy in the ordered state is ferromagnetic and in the disordered state shows spin glass behavior (Okazaki, 1995). $Ni_{0.50}Mn_{0.50}$ alloy is antiferromagnetic (Cable *et al*, 1994).

2. Numerical simulation

To determine short-range order in the disordered system, we apply the method recently proposed by Miyanaga *et al*. (Miyanaga, Okazaki, Babanov, *et al*., (1999)). The method is reduced to a solution of a system of linear algebraic equations for partial coordination numbers. We formulate the problem in a single scattering approximation. As input data we use first-nearest-neighbour (1NN) partial interatomic distances and Debye-Waller factors obtained independently from Mn and Ni K-edge EXAFS spectra in the binary alloy. We performed numerical simulations of EXAFS spectra of the ordered $Ni_{0.75}Mn_{0.25}$ alloy using code FEFF-8 (Ankudinov *et al*., 1998). From Table 1 it is seen that the influence of the multiple scattering (MS) contribution on the coordination numbers for the first shell is small, but for the second shell it is important. In order to obtain information about the second shell, using our single scattering approximation, it is necessary to first remove the MS contribution from the experimental data. This can be done when the structure is known, as is the case, for the ordered $Ni_{0.75}Mn_{0.25}$ alloy (Table 1, Exp. (MS-rmvd)). The MS-contribution can also be removed from the disordered state when a suitable structural model exists as indicated by the results listed in Table 1.

Table 1
Coordination numbers for ordered and disordered $Ni_{0.75}Mn_{0.25}$ alloys

	Ni-Ni		Ni-Mn		Mn-Ni		Mn-Mn	
shells	1	2	1	2	1	2	1	2
Ordered state								
model	8	6	4	0	12	0	0	6
MS–simulation	8.07	4.91	3.93	1.09	12.13	3.62	0.06	2.74
Exp.	7.59	4.31	4.38	1.48	12.88	5.03	-0.88	0.97
Exp. (MS-rmvd)	7.97	5.93	4.00	0.06	11.79	0.21	0.21	5.79
Disordered state								
model	9	4.5	3	1.5	9	4.5	3	1.5
Exp.	8.92	2.06	3.04	3.94	9.07	10.67	2.92	-4.67
Exp. (MS-rmvd)	9.29	4.52	2.68	1.48	8.58	4.58	3.42	1.41

For an unknown structure, we propose the following procedure: a) determine the partial interatomic distances and the coordination numbers for the first shell; b) construct a 3D model of the atomic arrangement for the cluster from 1000 atoms using a modification (proposed by Babanov's group) of the Reverse Monte-Carlo method to obtain the 1NN distances and coordination numbers; c) calculate the MS contribution with FEFF; d) after removing the MS contribution from experimental data, determine coordination numbers for the different shells by the method of Miyanaga, Okazaki, Babanov, and Ryazhkin. This scheme is applied in section 3.2 to ordered and disordered Ni–Mn alloys.

3. Experimental and results

Disordered $Ni_{0.75}Mn_{0.25}$ and $Ni_{0.80}Mn_{0.20}$ samples were prepared by quenching in ice water after heating at 650 C for 0.5 hour. Ordered samples were prepared by annealing in Ar at 400 C for 200 hours. All samples were ground to fine powders (38 μm). The disordered $Ni_{0.50}Mn_{0.50}$ sample was prepared as a foil with thickness 20 μm by shearing the ordered $Ni_{0.50}Mn_{0.50}$ sample under high pressure.

The K-edge absorption spectra of $Ni_{0.75}Mn_{0.25}$ and $Ni_{0.80}Mn_{0.20}$ samples for Ni and Mn were recorded in transmission mode at BL7C at the Photon Factory in Tsukuba. A Si(111) double crystal monochromator was used. The storage ring was operated at 2.5 GeV and the ring current was 200–300

mA. The K-edge absorption spectra of $Ni_{0.50}Mn_{0.50}$ for Ni and Mn were recorded in transmission mode at BL20ID–B (Heald *et al.*, 1999) at the Advanced Photon Source, Argonne National Laboratory. A Si(111) double crystal monochromator was used (65% tune at 200 eV above each K-edge absorption edge). The storage ring was operated at 7.0 GeV and ring current was 65-100mA .

EXAFS spectra (as shown in Fig.1) were measured in transmission mode for the powder and foil samples. The powder spectra suffer from the inhomogeneity, thickness and fluorescence effects. The spectra from the thick foils suffer from the thickness inhomogeneity effect and, to lesser extent, from the contribution of the fluorescent radiation from the sample being detected by the ionization chambers used in the transmission measurements. These effects were corrected using a new method (Ryazhkin *et al*., this volume).

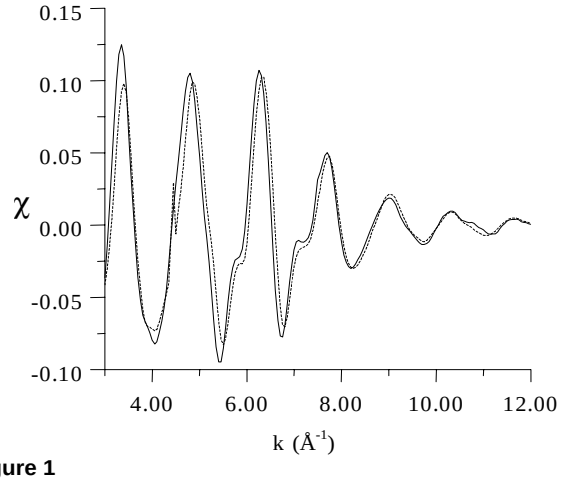

Figure 1
EXAFS spectra after correction for Ni K- (solid line) and Mn K-edge (dashed line) for $Ni_{0.50}Mn_{0.50}$ alloys.

We find the interatomic distances in $Ni_{0.75}Mn_{0.25}$ and $Ni_{0.80}Mn_{0.20}$ to be equal with R1NN = 2.53 ± 0.01 Å and R2NN = 3.57 ± 0.01 Å. In $Ni_{0.50}Mn_{0.50}$ alloys in both the ordered and disordered states R1NN = 2.57 ± 0.01 Å and R2NN = 2.64 ± 0.01 Å. No lattice distortion from cubic was evident from the EXAFS analysis.

In Table 2 we compare the coordination numbers determined from experimental data with the known information for the ordered Ni_3Mn and $Ni_{0.50}Mn_{0.50}$ alloys (Hansen *et al*. (1958)) and coordination numbers obtained from numerical calculations using a statistical model for the disordered state. Ordering of the $Ni_{0.80}Mn_{0.20}$ alloy (Hansen *et al*. (1958)) produces the Cu_3Au structure type where Mn atoms occupy the Au positions as in Ni_3Mn and "excess" Ni atoms randomly occupy the Au position. $Ni_{0.50}Mn_{0.50}$ has a lattice similar to that of CuAu alloy. We find that the coordination numbers for disordered state Ni-Mn alloys are close to the ones calculated with the statistical model. For $Ni_{0.50}Mn_{0.50}$ alloy we can consider it is necessary to take account to coordination numbers for two closely spaced spheres .

The magnetic properties of Ni_xMn_{1-x} (Satoh, *et al*, 1978, Miyanaga, Okazaki, Aono *et al*., 1999) have been classified into three types according to the numbers of first nearest neighbor Mn atoms around a Mn atom (n): Ni-Mn alloys under the condition (A) that $n \leq 2$ show ferromagnetic behavior; (B) that for $n = 3$ exist in a weak molecular field and form a spin glass at low temperature; (C) that for $n \geq 4$ show antiferromagnetic behavior. Using the EXAFS coordination numbers obtained in the present paper, we have classified the magnetic behavior of the NiMn alloys studied and tabulated the classification in Table 3.

Table 2. Coordination numbers for two shells of Ni-Mn alloys

alloy	Ni-Ni, at		Ni-Mn, at		Mn-Ni, at		Mn-Mn, at	
shells	1	2	1	2	1	2	1	2
$Ni_{75}Mn_{25}$ (model of the ordered state)	8	6	4	0	12	0	0	6
$Ni_{75}Mn_{25}$ (t_{ann} = 200 h)	7.97	5.93	4.00	0.06	11.79	0.21	0.21	5.79
$Ni_{75}Mn_{25}$ (model of the disordered state)	9.00	4.50	3.00	1.50	9.00	4.50	3.00	1.50
$Ni_{75}Mn_{25}$ (t_{ann}= 0 h)	9.29	4.52	2.68	1.48	8.58	4.58	3.42	1.41
$Ni_{80}Mn_{20}$ (model of the ordered state)	9.00	6.00	3.00	0.00	12.00	1.22	0.00	4.78
$Ni_{80}Mn_{20}$ (t_{ann} = 200 h	9.15	6.44	2.85	-0.45	12.05	1.75	-0.05	4.25
$Ni_{80}Mn_{20}$ (model of the disordered state)	9.60	4.80	2.40	1.20	9.60	4.80	2.40	1.20
$Ni_{80}Mn_{20}$ (t_{ann} = 0 h)	9.54	4.74	2.43	1.25	9.86	4.86	2.15	1.14
$Ni_{50}Mn_{50}$ (model of the ordered state)	0.00	4.00	8.00	0.00	8.00	0.00	0.00	4.00
$Ni_{50}Mn_{50}$ (the ordered state)	–0.14	3.62	8.16	0.35	8.16	0.36	–0.17	3.65
$Ni_{50}Mn_{50}$ (model of the disordered state)	4.00	2.00	4.00	2.00	4.00	2.00	4.00	2.00
$Ni_{50}Mn_{50}$ (the disordered state)	3.99	1.92	4.01	2.03	4.01	2.01	4.00	1.99

Table 3. Classification of the magnetic behavior of the Ni-Mn alloys

alloy	$Ni_{75}Mn_{25}$		$Ni_{80}Mn_{20}$		$Ni_{50}Mn_{50}$	
state	ordered	disordered	ordered	disordered	ordered	disordered
Magn. behavior	A	B	A	AB	C	C

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