Short-range order in β_1-MnZn alloys as investigated by the NMR of ^{55}Mn nuclei

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NMR spectra of ^{55}Mn in five compositions of β_1-MnZn alloys have been studied. The various satellite signals observed in all these compositions have been attributed as arising due to occupancy of Mn and Zn atoms in Zn and Mn sites, respectively. The signals have been analyzed using a phenomenological model in which it is assumed that the Mn interaction with the Mn in the first coordination shell is repulsive and that with Zn in the second and third coordination shells is attractive.

INTRODUCTION

The problem of short-range order (SRO) has become a subject of great interest in recent years. Hyperfine interactions are known to be an accurate means of investigating SRO in dilute alloys.[1] The SRO parameters can be obtained by NMR at the impurity site embedded in a host lattice. The satellites observed in such systems can be attributed to various pair and triplet interactions. Such studies have been carried out in various binary dilute alloys $FeCo$,[2] $FeMn$,[3] FeI (I:P, Ga, As, Sb) and ternary alloys such as $FeSbM$ (M:Ni, Cr).[4] However, SRO studies have only been carried out in a few concentrated alloys. For example, in FeCo, which exists over a wide concentration range, Muraoka *et al.*[5] have been able to observe satellite lines corresponding to ^{57}Co in $Fe_{50}Co_{50}$ arising due to the effect of first-, second-, and third-nearest neighbors.

The alloy MnZn, which exists in several crystallographic and magnetic phases, has been studied by various authors.[6-11] Perhaps particular emphasis was given to the β_1 phase due to its interesting magnetic properties. Hihara *et al.*[9,10] studied the NMR of ^{55}Mn and ^{67}Zn resonances, whereas Hori and Nakagawa[11] reported the magnetization measurements. The electrical properties and the magnetization studies of this phase over a wide concentration range were reported by us earlier.[12] In this paper we report the results of the NMR investigations of ^{55}Mn carried out in ferromagnetic β_1-MnZn alloys.

PREPARATION AND CHARACTERIZATION

MnZn alloys having formal compositions $Mn_{54}Zn_{46}$, $Mn_{50}Zn_{50}$, $Mn_{46}Zn_{54}$, $Mn_{42}Zn_{58}$, and $Mn_{36}Zn_{64}$ were prepared using 99.99% pure Mn and Zn following the procedure reported elsewhere.[12] All the compositions were characterized by x-ray diffraction and magnetization studies. An externally quenched super-regenerative oscillator working in the range 80–360 MHz was employed for the detection of ^{55}Mn resonances.

EXPERIMENTAL RESULTS AND ANALYSIS

The NMR signals from ^{55}Mn nuclei recorded at 300 K in β_1-MnZn alloys of various concentrations are shown in

Fig. 1. The spectra of β_1-$Mn_{46}Zn_{54}$ shows one main signal at 184.3 MHz and a few additional signals (satellites) spread over a frequency range of 13 MHz on either side of the main signal. A phenomenological model has been used to analyze the NMR spectra in β_1-MnZn alloys considering various nearest- and next-nearest-neighbor interactions.

In a solid solution of stoichiometric β_1-$Mn_{50}Zn_{50}$ alloy, the Zn atoms occupy the center of the cube and the Mn atoms occupy the corners and form a bcc CsCl-type structure. Each Mn atom is surrounded by 8 atoms of Zn and 6 and 12 atoms of Mn in the first-, second-, and third-coordination shells, respectively, as shown in Fig. 2.
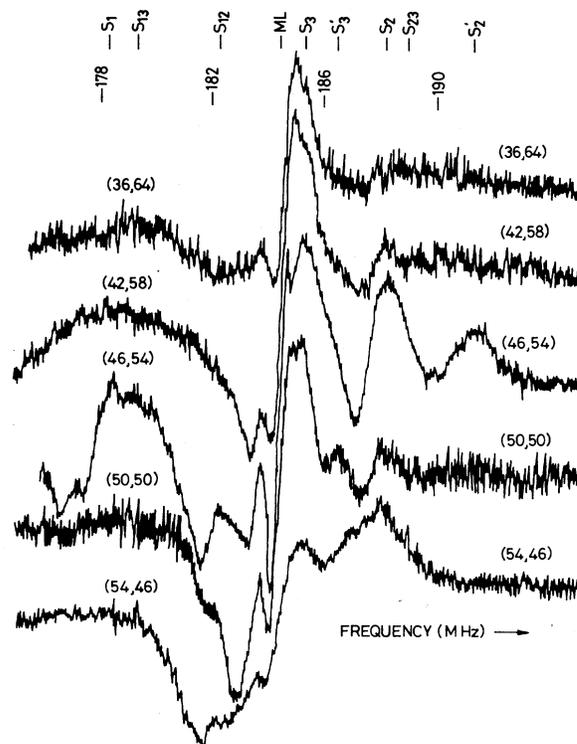

FIG. 1. NMR of ^{55}Mn spectra in β_1-MnZn alloys of various compositions at 300 K.
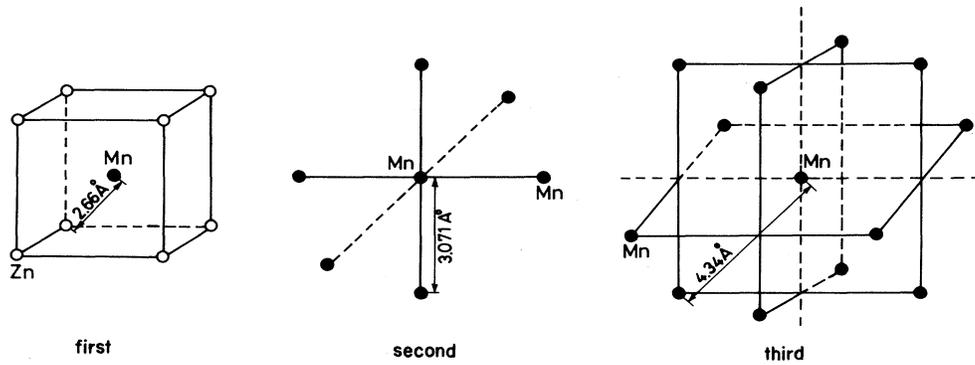
FIG. 2. Configuration of various nearest- and next-nearest neighbors around the Mn atom in β_1-MnZn.

The satellite lines arise due to some of the Mn atoms occupying the Zn sites, and some of the Zn atoms occupying the Mn sites; giving different configurations at the Mn atoms under consideration. As a consequence, when looking for NMR signals, these wrongly occupied atoms give rise to various satellite signals belonging to pair and triplet interactions. The probability for wrong occupation in MnZn alloy systems is due more to their nearly equal atomic dimensions. In this description it has been assumed that beyond the third-neighbor shell, the hyperfine field is insensitive to the site occupation. Therefore, the wrongly occupied atoms beyond the third-coordination shell will no longer give rise to resolved satellite signals but may be responsible for line broadening.

PHENOMENOLOGICAL MODEL

The hyperfine field is divided into two components, viz. a local contribution and a nonlocal contribution. A local contribution, which is also known as self-field, H_{self}, arises due to the conduction-electron polarization and the core polarization by the local moments of the resonant nuclei. A nonlocal contribution, which is also known as transferred hyperfine field, H_{trans}, arises due to the conduction-electron polarization by the moment of surrounding atoms through the electronic environment.[13]

The magnitude of the transferred hyperfine field can be written as

$$H_{trans} = n_1 H_t^1 + n_2 H_t^2 + N_3 H_t^3 + \cdots , \qquad (1)$$

where n_1, n_2, and n_3 are the number of atoms in the first-, second-, and third-coordination shells, and H_t^1, H_t^2, and H_t^3 are the transferred hyperfine fields from the respective neighboring shells.

The magnitude of total hyperfine field in β_1-MnZn can be written as

$$H_{tot} = H_{hf}(0) = H_{self} + 8H_{Zn}^1 + 6H_{Mn}^2 + 12H_{Mn}^3 , \qquad (2)$$

where $H_{hf}(0)$ represents the field corresponding to the main line occurring at 184.3 MHz. The possible atomic configurations can be written by assuming the wrong occupancy (which are underlined) in the neighboring shells as

$$H_{hf}(1) = H_{self} + \underline{1H_{Mn}^1} + \underline{7H_{Zn}^1} + 6H_{Mn}^2 + 12H_{Mn}^3 ,$$

$$H_{hf}(2) = H_{self} + 8H_{Zn}^1 + \underline{1H_{Zn}^2} + \underline{5H_{Mn}^2} + 12H_{Mn}^3 , \qquad (3)$$

$$H_{hf}(3) = H_{self} + 8H_{Zn}^1 + 6H_{Mn}^2 + \underline{1H_{Zn}^3} + \underline{11H_{Mn}^3} .$$

These equations correspond to the near-neighbor pair interactions S_1, S_2, and S_3, and the positions of the satellite lines corresponding to these interactions are shown in Table I.

The triplet interactions can also be written by considering the wrong occupancy in two different neighboring shells as

TABLE I. Positions of the satellite lines corresponding to various nearest-neighbor pair interactions in β_1-Mn$_{46}$Zn$_{54}$.

| | Nearest-neighbor pair interactions | | | Resonance signal (MHz) | $\Delta\nu$ (MHz) | Assignment of the signal |
	First	Second	Third			
Mn	8Zn	6Mn	12Mn	184.3		Main line
	7Zn 1Mn	6Mn	12Mn	178.3	−6.0	S_1
	8Zn	5Mn 1Zn	12Mn	188.0	+3.7	S_2
	8Zn	6Mn	11Mn 1Zn	185.3	+1.0	S_3

$$H_{hf}(4) = H_{self} + 2H_{Mn}^1 + \underline{6H_{Zn}^1} + 6H_{Mn}^2 + 12H_{Mn}^3 \; ,$$

$$H_{hf}(5) = H_{self} + 8H_{Zn}^1 + \underline{2H_{Zn}^2} + \underline{4H_{Mn}^2} + 12H_{Mn}^3 \; ,$$

$$H_{hf}(6) = H_{self} + 8H_{Zn}^1 + 6H_{Mn}^2 + \underline{2H_{Zn}^3} + 10H_{Mn}^3 \; ,$$

$$H_{hf}(7) = H_{self} + \underline{1H_{Mn}^1} + \underline{7H_{Zn}^1}$$
$$+ \underline{1H_{Zn}^2} + \underline{5H_{Mn}^2} + 12H_{Mn}^3 \; ,$$

$$H_{hf}(8) = H_{self} + \underline{1H_{Mn}^1} + \underline{7H_{Zn}^1} + 6H_{Mn}^2$$
$$+ \underline{1H_{Zn}^3} + 11H_{Mn}^3 \; ,$$

$$H_{hf}(9) = H_{self} + 8H_{Zn}^1 + \underline{1H_{Zn}^2} + \underline{5H_{Mn}^2}$$
$$+ \underline{1H_{Zn}^3} + 11H_{Mn}^3 \; .$$

(4)

In order to assign various satellite signals observed in β_1-Mn$_{46}$Zn$_{54}$ alloy, the following assumptions have been made.

(a) The interaction of Mn with the first-nearest-neighbor Mn is considered to be repulsive.

(b) The interaction of Mn with Zn in the second- and third-nearest neighbor is considered to be attractive.

Using the first assumption, the signal occurring on the lower-frequency side of the spectrum at 178.3 MHz can be attributed to the interaction of Mn with an Mn occupying the first-nearest-neighbor position (S_1). Similarly, the signals occurring at 188.0 and 185.3 MHz are due to the interaction of Mn with Zn atoms occupying the second- (S_2) and third- (S_3) nearest-neighbor positions, respectively. The assignment of these pair interactions is also given in Table I.

Taking the positions of S_1, S_2, and S_3 signals, various possible positions of the satellite signals corresponding to the nearest-neighbor triplet interactions have been calculated and are shown in Table II. In this table, for example, S_{12} refers to an atom occupying the Zn site in the first-nearest-neighbor shell and also a Zn atom occupying an Mn site in the second-nearest neighbor shell. Similarly S_2 represents two Zn atoms occupying second-

nearest-neighbor positions and so on.

The signal corresponding to S_1' could not be seen anywhere around 172 MHz, and the signal corresponding to S_{23} could not be resolved probably because it would have been merged with S_2 signal. The assignment of various satellite signals to different triplet interactions is fairly good. However, no other assignment led to a correct assignment of the triplet interactions.

The NMR spectra of ^{55}Mn in β_1-Mn$_{36}$Zn$_{64}$, β_1-Mn$_{42}$Zn$_{58}$, β_1-Mn$_{50}$Zn$_{50}$, and β_1-Mn$_{54}$Zn$_{46}$ which is shown in Fig. 1, have also been analyzed and the positions of the satellite lines have been assigned to various nearest-neighbor pair and triplet interactions.

DISCUSSION

The main signal occurring at 184.3 MHz in all the β_1-MnZn alloys is attributed to Mn and Zn atoms occupying their respective sites. The satellite signals arise due to the wrong occupation of both Mn and Zn atoms in place of Zn and Mn sites. There is an evidence of such observation of satellite signals in binary alloys of Fe$_{50}$Co$_{50}$, Fe$_{50}$V$_{50}$, and Fe$_{50}$Rn$_{50}$ having the same bcc type structure.[13] Muraoka et al.[5] also observed satellite signals in various concentrated alloys of Fe$_{50}$Co$_{50}$, Fe$_{48}$Co$_{52}$, and Fe$_{52}$Co$_{48}$ having the same bcc type structure. They observed one main signal and two satellite signals, one occurring at the lower-frequency side corresponding to Co interaction with Co in the first-nearest-neighbor position and the other at higher-frequency side corresponding to the Co interaction with Fe in the second-nearest-neighbor position.

In dilute alloy of *Fe*Mn, also belonging to a bcc structure, Pierron et al.[3] reported the Mn-Mn pair interaction in the first- and second-nearest-neighbor positions to be repulsive and at the third-coordination shell the Mn-Mn pair interaction is an attractive one. It was also reported that the first-nearest-neighbor interactions between Co atoms, V atoms, and Cr atoms in an Fe matrix is repul-

TABLE II. Positions of the satellite lines corresponding to various nearest-neighbor triplet interactions in β_1-Mn$_{46}$Zn$_{54}$.

| | Nearest-neighbor triplet interactions | | | Resonance signals | | Assignment |
	First	Second	Third	Calculated (MHz)	Observed (MHz)	of the signals
Mn	7Zn <u>1Mn</u>	5Mn <u>1Zn</u>	12Mn	182.0	182.2	S_{12}
	7Zn <u>1Mn</u>	6Mn	11Mn <u>1Zn</u>	179.3	179.2	S_{13}
	8Zn	5Mn <u>1Zn</u>	11Mn <u>1Zn</u>	189.0		S_{23}
	6Zn <u>2Mn</u>	6Mn	12Mn	172.3		S_1'
	8Zn	4Mn <u>2Zn</u>	12Mn	191.7	191.5	S_2'
	8Zn	6Mn	10Mn <u>2Zn</u>	186.3	186.4	S_3'

sive.[14−19] Therefore, our first assumption that the Mn-Mn pair interaction in the first-coordination shell in β_1-MnZn alloys is repulsive is a valid one.

The pair interactions between nonmagnetic atoms were studied by various authors mostly in the case of ternary compounds.[4,20,21] The interaction between Sb and Ni atoms occupying the first- and second-coordination shell in an Fe matrix is an attractive one.[4,20] Similarly the pair interactions between Sn and Cr, Sb and Co, and Sb and Cr are also reported to be attractive.[20,21] Therefore, when an Mn atom is replaced by a Zn atom in the second- and third- coordination shells in β_1-MnZn alloys, it is reasonable to expect an attractive interaction giving rise to the occurrence of satellite signals (S_2 and S_3) at the higher-frequency side.

Since the number of atoms in the first, second, and third coordination shells are 8, 6, and 12, it is probable that the wrong occupation is more in third-, first-, and second-coordination shells, respectively. As the Mn interaction with Mn in the first-coordination shells is strongly a repulsive one, the probability for wrong occupation in this shell is small. On the other hand, the Mn interaction with Zn in the second-coordination shell is an attractive one, and therefore the probability for wrong occupation in this shell is probably more than the first one.

In β_1-Mn$_{46}$Zn$_{54}$ alloys the signals corresponding to S_1, S_2, S_3, S_{12}, S_{13}, S_2', and S_3' could be seen clearly. Since the probability of occupation of two Mn atoms in the first coordination is low, the satellite signals corresponding to S_1' could not be observed. Furthermore, the satellite signal corresponding to S_{23} could not be resolved probably because an intense and broad signal corresponding to S_2 appears around the same frequency.

In all the alloys other than β_1-Mn$_{46}$Zn$_{54}$ the spectra show a broad shoulder on the low-frequency side for Zn-rich compositions and the signals are smeared out below the noise level for Mn-rich compositions. This is probably because all the signals appearing on the low-frequency side are either pair or triplet interactions involving mainly the Mn-Mn atoms. It is also seen that the main signal gets broadened in the Mn-rich alloys. Such a line broadening was observed while studying the effect of magnetic impurities in MnSb.[22]

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