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Nuclear Magnetic Resonance Study of $MnAs_{1-x}P_x$

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Abstract

The Mn^{55} and As^{75} NMR in orthorhombic $MnAs_{1-x}P_x$ with $x = 0.03$, 0.05 and 0.10 have been observed by a standard spin echo method at 77 K. The Mn^{55} hyperfine field is distributed over the range from 145 to 165 kOe. The magnetic moment of 1.8 μ_B estimated from the hyperfine data suggests a low spin configulation of Mn atom as in orthorhombic MnAs.

The As^{75} hyperfine field of about 50 kOe is much smaller than a value of 283 kOe in hexagonal MnAs.

§ 1. Introduction

Ferromagnetic compound MnAs exhibits a change in the crystal structure from the hexagonal (NiAs) to the orthorhombic (MnP) type and a decrease in the saturation magnetization with application of hydrostatic pressure of about 4 kbar at 77 K.[1,2] Similar changes in the crystal structure and magnetization of MnAs take place also by substituting some amount of phosphorous atoms for arsenic atoms.[3-5] Goodenough et al.[1,3] explained the decrease of magnetization in the orthorhombic MnAs (stable at high pressure) and $MnAs_{1-x}P_x$ by assuming that the structural change is accompanied by a change in the Mn magnetic moment from a high spin of $3.5\mu_B$ to a low spin of $1.7\mu_B$. The neutron diffraction studies by Schwartz et al.[6,7] confirmed the similarity between the ordered magnetic structures of orthorhombic MnAs and orthorhombic $MnAs_{0.92}P_{0.08}$, but suggested that Mn atoms in orthorhombic MnAs have a high-spin configuration of $2.6\mu_B$.

In a previous work[8] the pressure-induced transition from the hexagonal to the orthorhombic phase in MnAs was investigated by means of nuclear magnetic resonance (NMR) technique. The Mn^{55} NMR was observed as a function of hydrostatic pressure, and it was shown that a sudden change in the Mn^{55} hyperfine field occurs at the hexagonal-orthorhombic phase transition.

Nuclear magnetic resonance studies of $MnAs_{1-x}P_x$ in the orthorhombic phase hav been made in order to investigate the similarity between the high pressure phase of MnAs and orthorhombic $MnAs_{1-x}P_x$ from the microscopic point of view. In this report results of the Mn^{55} and As^{75} NMR measurements in $MnAs_{1-x}P_x$ are given in comparison with the NMR data in hexagonal and orthorhombic MnAs.

§ 2. Experimental

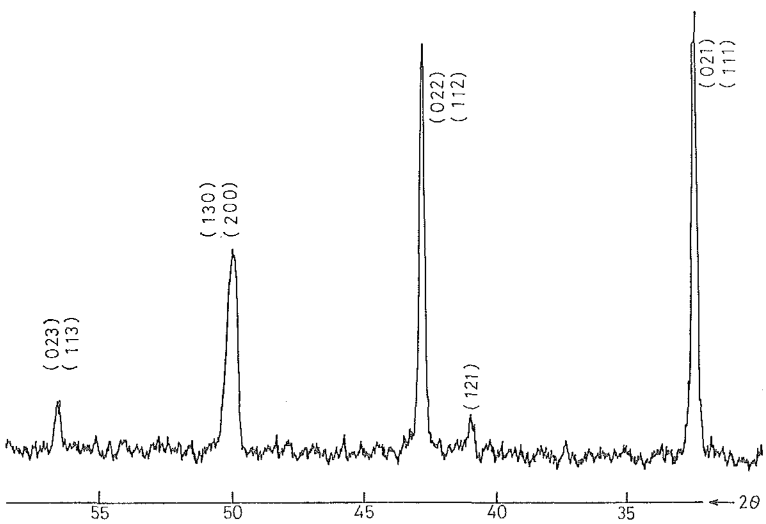

Fig. 1 : The diffraction pattern in $MnAs_{0.97}P_{0.03}$ at room temperature.

The compounds $MnAs_{1-x}P_x$ with $x=0.03$, 0.05 and 0.10 were prepared by melting a desired proportion of the constituent elements in a quartz ampule. The product was ground into powder, which was annealed in vacuum for one day at 400°C. The x ray analysis of the specimens was made, and it was confirmed that all the specimens have the crystal structure of orthorhombic (MnP) type described by Ido.[4] A typical powder pattern of $MnAs_{0.97}P_{0.03}$ is shown in Fig. 1, and the crystal structure of orthorhombic type is shown in the

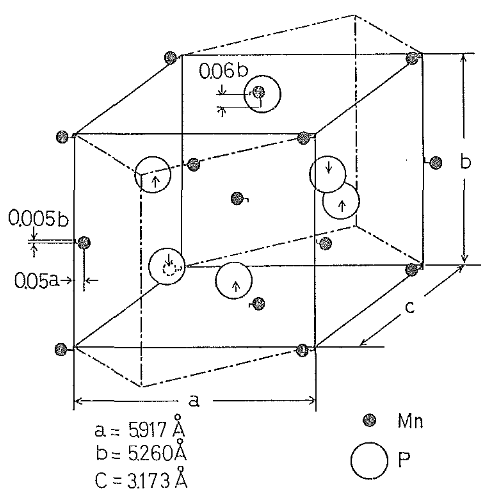

Fig. 2 : Orthorhombic B31 structure of MnP showing its relationship to hexagonal $B8_1$ structure.

relationship to that of hexagonal type in Fig. 2.

The NMR measurements were made by means of a conventional spin echo method at 77 K. The amplitude of the spin echo following two rf pulses was observed as a function of frequency.

§ 3. Experimental Results and Discussions

The Mn^{55} and As^{75} NMR spectra in hexagonal MnAs at 77 K are shown in Fig. 3 (a). The Mn^{55} NMR occurs at 235 MHz and consists of quadrupole-split five lines with a value of $e^2qQh^{-1} = 23$ MHz. The As^{75} NMR consists of three component lines centered at 206 MHz with a value of $e^2qQh^{-1} = 16$ MHz. The hyperfine fields at Mn^{55} and As^{75} nuclei are 223 and 283 kOe, respectively. In $MnAs_{1-x}P_x$ the Mn^{55} and As^{75} NMR, which are observed in hexagonal MnAs, disappeared for $x \geqq 0.03$, and two new NMR lines were observed in the frequency ranges from 140 to 180 MHz and from 25 to 45 MHz. The NMR spectra in $MnAs_{0.97}P_{0.03}$ at 77 K are shown in Fig. 3 (b). The resonance frequency and lineshape of the higher-frequency NMR is very similar to those of the Mn^{55} in the high-pressure phase of MnAs, where the lineshape of the Mn^{55} NMR is interpreted as that broadened by an electric quadrupole and anisotropic interactions.[8] From the similarity between the NMR in orthorhombic MnAs and $MnAs_{0.97}P_{0.03}$ the higher-frequency NMR is attributed to Mn^{55} nuclei, although the quadrupole splitting is not well-resolved, and the lower-frequency NMR may be attributed to As^{75} nuclei. The NMR spectra in $MnAs_{0.95}P_{0.05}$ and $MnAs_{0.90}P_{0.10}$ are shown in Fig. 3 (c) and (d). When the concentration of phosphorous atoms was further increased, the shape of the NMR spectra was little changed, and the NMR frequency slightly shifted to lower frequencies.

Recently Haneda et al.[9] investigated the magnetic structure of $MnAs_{0.92}P_{0.08}$ by means of neutron diffraction and proposed a double spiral spin structure in which the Mn magnetic moments of $(2.0 \pm 0.4)\ \mu_B$ are arranged in a spiral propagating along the c axis with a turn angle of 20°. In this structure the Mn moments rotate within the bc plane, and, therefore, the quantization axis of the nuclear spin varies from site to site as in domain walls of a ferromagnet. This results in a distribution of the NMR frequency in the presence of an electric quadrupole and anisotropic hyperfine interaction. The observed Mn^{55} and As^{75} NMR in $MnAs_{1-x}R_x$ are explained as such a distribution of the NMR frequency. A similar spectrum was also reported for the Mn^{55} NMR in isostructural compound Mnp.[10]

In the previous paper[8] the Mn^{55} hyperfine fields for the magnetic moments parallel to the b and c axes in orthorhombic MnAs were obtained to be 165 and 145 kOe, respectively, from the frequencies of the central components of the

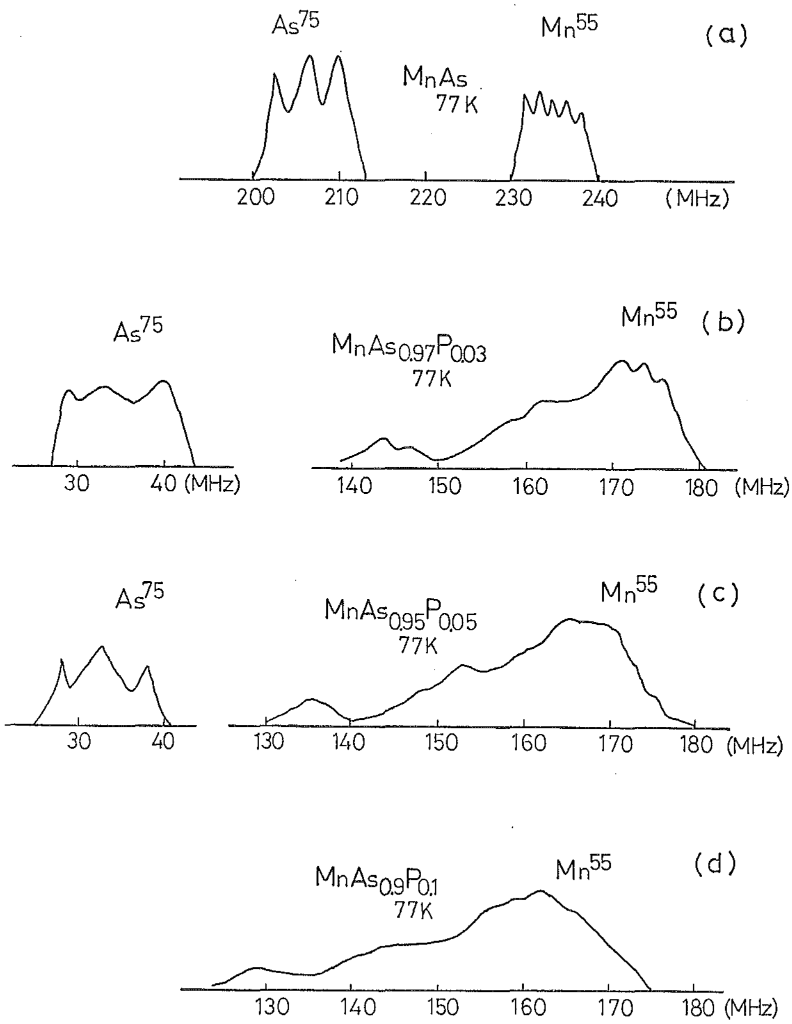

Fig. 3 : The Mn^{55} and As^{75} NMR spectra observed by spin echo method at 77 K.

quadrupole-split lines. In addition, the magnetic moments along the b and c axes were estimated to be 1.9 and $1.7\mu_B$, respectively, by comparing the NMR and magnetic data with those in MnP. In the case of $MnAs_{1-x}P_x$ the Mn^{55} hyperfine fields are not accurately determined, since the electric quadrupole splittings are not resolved. But nearly same distributions of the NMR frequency in both orthorhombic MnAs and $MnAs_{0.97}P_{0.03}$ suggest that the Mn^{55} hyperfine field and magnetic moment in $MnAs_{0.97}P_{0.03}$ are nearly equal to those in orthorhombic MnAs.

As for the As^{75} NMR the hyperfine field at As^{75} nuclei in $MnAs_{0.97}As_{0.03}$ is about 50 kOe, which is much smaller than the value of 283 kOe in hexagonal MnAs. The hyperfine field at nonmagnetic As^{75} nuclei may primarily come from the exchange polarization of outer 5s electrons due to neighboring Mn spins. The observed decrease in the As^{75} hyperfine field, however, cannot be fully explained by the decrease in Mn magnetic moment (from 3.5 to 1.8 μ_B). Most part of the decrease in the hyperfine field is due to the decrease in the Mn magnetic moment. The remaining might be due to the noncollinear arrangement of neighboring Mn spins in the spiral spin structure.

In conclusion the Mn^{55} NMR results suggest that Mn atoms in $MnAs_{1-x}P_x$ are in a low spin state of about 1.8 μ_B as in orthorhombic MnAs and provide a microscopic evidence for the similarity between $MnAs_{1-x}P_x$ and high-pressure phase of MnAs, which was referred to by previous workers.[3,6]

The As^{75} NMR results give a small hyperfine field at As^{75} nuclei and suggest that $MnAs_{1-x}P_x$ have a noncollinear arrangement of Mn magnetic moments.

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References

1) J. B. Goodenough and J. A. Kafalas : Phys. Rev. 157 (1967) 389.
2) M. Menyuk, J. A. Kafalas, K. Dwight and J. B. Goodenough : Phys. Rev. 177 (1969) 942.
3) J. B. Goodenough, D. H. Ridgley and W. A. Newman : Proc. Intern. Conf. Magnetism, Nottingham (1964) 542.
4) H. Ido and T. Suzuki : J. Phys. Soc. Japan 24 (1968) 964.
5) M. M. Rodger and R. Fruchart : Mat. Res. Bull. 3 (1968) 253.
6) E. L. Hall, L. H. Schwartz, G. P. Felcher and D. H. Ridgley : J. appl. Phys. 41 (1970) 939.
7) L. H. Schwaltz, E. L. Hall and G. P. Felcher : J. appl. Phys. 42 (1971) 1621.
8) H. Yoshie and T. Hihara : J. Phys. Soc. Japan 40 (1976) 427.
9) T. Haneda, N. Kazama, Y. Yamaguchi and H. Watanabe : private communication.
10) H. Nagai, T. Hihara and E. Hirahara : J. Phys. Soc. Japan 29 (1970) 622.