

## Mössbauer and Susceptibility Investigation of Manganese-Tin Alloys with the Beta-Manganese Structure\*

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Mössbauer and magnetic measurements have been made for manganese-tin alloys with the  $\beta$ -Mn structure. Tin is found to predominantly occupy type-II sites. The  $\text{Sn}^{119}$  isomer shift in alloys containing 2.5-, 5.0-, and 8.0-at.-% tin is  $+2.02 \pm 0.02$  at type-I sites and  $+1.70 \pm 0.02$  mm/sec at type-II sites (relative to  $\text{BaSnO}_3$  at 300°K). While there is very little change in the isomer shift with concentration, the average magnetic moment per Mn atom is reduced by  $\sim 20\%$  at 8.0-at.-% Sn. Any change upon alloying that leads to an instability of the  $\beta$ -Mn phase is not reflected in changes in the electronic structure of solute tin atoms.

### INTRODUCTION

THE present study examines the concentration dependence of the isomer shift and quadrupole coupling of  $\text{Sn}^{119}$  in manganese-tin alloys with the  $\beta$ -Mn structure. Also, magnetic measurements were made to monitor the change in effective moment of the Mn atoms in the same alloys.

The stability of the  $\beta$ -Mn structure was studied by Bardos *et al.*, for alloys of manganese with transition and group-IV nontransition elements.<sup>1</sup> Elongated phase fields were found that require, for the preservation of the Hume-Rothery rule for the average electron concentration in this "electron phase," an effective valence of nine electrons per tin or germanium atom. Bardos *et al.* explained their results on the basis of a model in which the itinerant  $d$  electrons of Mn are excluded from Ge and Sn sites because of orthogonality requirements with respect to the closed  $d$ -shell electrons of the Sn and Ge atoms.<sup>1</sup> Their model assumes that the  $5d$  ( $4d$ ) levels of Sn (Ge) do not lie below the Fermi surface of the alloy.

Solute Sn atoms undergo drastic changes in "available volume" when dissolved in transition elements.<sup>2</sup> The atomic volume available to the Sn atom in the  $\beta$ -Mn structure is 40% less than that in semiconducting  $\alpha$ -Sn and 20% less than that in metallic  $\beta$ -Sn. If this change in volume is due to compression, the change in isomer shift should be proportional to the change in volume. To further elucidate the electronic structure of alloys with the  $\beta$ -Mn type structure, the Mössbauer isomer shift and quadrupole splitting at  $\text{Sn}^{119}$  nuclei were

measured and the behavior of the effective magnetic moment of Mn atoms were determined.

### EXPERIMENTAL

The solid solubility limit of tin in  $\beta$ -Mn was reported to be 8.7 at.-%.<sup>3</sup> Alloys of 2.5-, 5.0-, and 8.0- at.-% tin were prepared by the method described by Bardos *et al.*<sup>1</sup> Powder x-ray patterns showed that the alloys were single phase and had the  $\beta$ -Mn ( $P4_32-O_7$ ) structure.

For the Mössbauer measurements, the source matrix for  $\text{Sn}^{119}$  was  $\text{BaSnO}_3$  at 300°K. The width (full width at half-maximum) of each component of the quadrupole doublet of the absorption spectrum of  $\beta$ -Sn at 300°K was 0.74 mm/sec; the isomer shift was  $+2.54 \pm 0.01$  mm/sec.

### DISCUSSION

The crystal structure of  $\beta$ -Mn is cubic with 20 atoms per unit cell.<sup>4</sup> There are two nonequivalent sites: eight type-I and 12 type-II. Atoms in both sites have a nominal coordination of twelve but with varied interatomic distances, as illustrated in Table I<sup>5</sup>; the mean

TABLE I. Variation of interatomic distances and type of neighbor for nonequivalent sites in  $\beta$ -Mn (after Kripyakevich, Ref. 5).

Type and occupation number	Neighbors	Interatomic distances
I 8	3 Mn I 3+3+3 Mn II	2.36 2.53, 2.67, 2.67
II 12	2+2+2 Mn I 2+4 Mn II	2.53, 2.67, 2.67 2.61, 2.65

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<sup>1</sup> D. I. Bardos, R. K. Malik, F. X. Spiegel, and Paul A. Beck, Trans. Met. Soc. AIME 236, 40 (1960).

<sup>2</sup> T. Yoshioka and Paul A. Beck, Trans. Met. Soc. AIME 233, 1789 (1965).

<sup>3</sup> H. Nowotny and K. Schubert, Z. Metallk. 37, 17 (1946).

<sup>4</sup> G. D. Preston, Phil. Mag. 5, 1198 (1928).

<sup>5</sup> P. I. Kripyakevich, Kristallografiya 5, 273 (1960) [Soviet Phys. Cryst. 5, 253 (1960)].

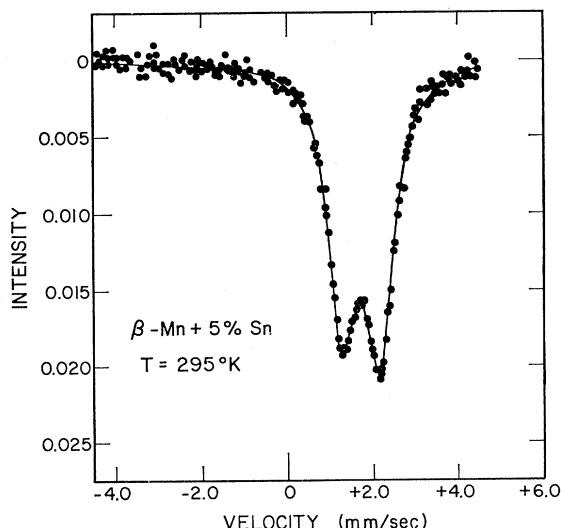


FIG. 1. Mössbauer absorption pattern for 5% Sn in  $\beta$ -Mn at 300°K. The source is  $\text{Sn}^{119m}$  in  $\text{BaSnO}_3$  at 300°K. The solid line is a least-squares fit to the model described in the text.

radius of Mn in type-II sites is  $\sim 11\%$  larger than that of Mn in type-I sites. Both sites have lower than cubic symmetry; Drain has calculated that the ratio of the quadrupole coupling at type-II Mn atoms is about five times that at type-I Mn atoms and, further, that this ratio is very sensitive to small changes in atomic distances.<sup>6</sup>

The Mössbauer spectrum for the 5.0-at.% Sn alloy at 300°K is shown in Fig. 1; the spectra for the 2.5 and 8.0-at.% alloys are similar. On the basis of size considerations and occupation numbers, Sn atoms are expected

to preferentially occupy the larger type-II sites. Imposing the constraint that the ratio of the intensities of the subspectra for Sn atoms in type-II sites to Sn atoms in type-I sites should have at least the ratio expected on the assumption of random occupation of sites, the Mossbauer parameters given in Table II were obtained.

There is predominant occupation of the larger site II by the Sn atoms. The isomer shift changes very slightly, if at all, as the tin concentration is varied toward the solubility limit. Moreover, the value of the shift is very close to that of  $\alpha$ -Sn and corresponds to an electronic structure for Sn in  $\beta$ -Mn of nearly  $s^1p^3$ . Atomic calculations show that  $d$  admixing would have only a slight effect on the isomer shift.<sup>7</sup> If, however, the reduction of 40% in available volume is caused by compression of the Sn atom, the occupation of the 5s band could be greater than one electron since pressure experiments show that the isomer shift for  $\text{Sn}^{119}$  decreases with decreasing volume in  $\beta$ -Sn.<sup>8</sup> We note that the isomer shift for  $\text{Sn}^{119}$  in  $\beta$ -Mn falls between the values for the  $\text{Sn}^{119}$  in Cu or vanadium-base alloy phases for which the volume available to the Sn atom decreases relative to  $\alpha$ -Sn by 35.4 and 45.1%, respectively.<sup>2</sup> However, the isomer shifts for Sn at both sites do not reflect the increase in volume ( $\sim 10\%$ ) of the alloys as the tin concentration increases to 8%.

There is very little evidence in the concentration dependence of the shift for the participation of Sn in any possible electronic changes in these alloys; a similar conclusion is inferred from the quadrupole splitting. The splitting at type-II sites is not composition-dependent. The splitting at type-I sites is reduced slightly

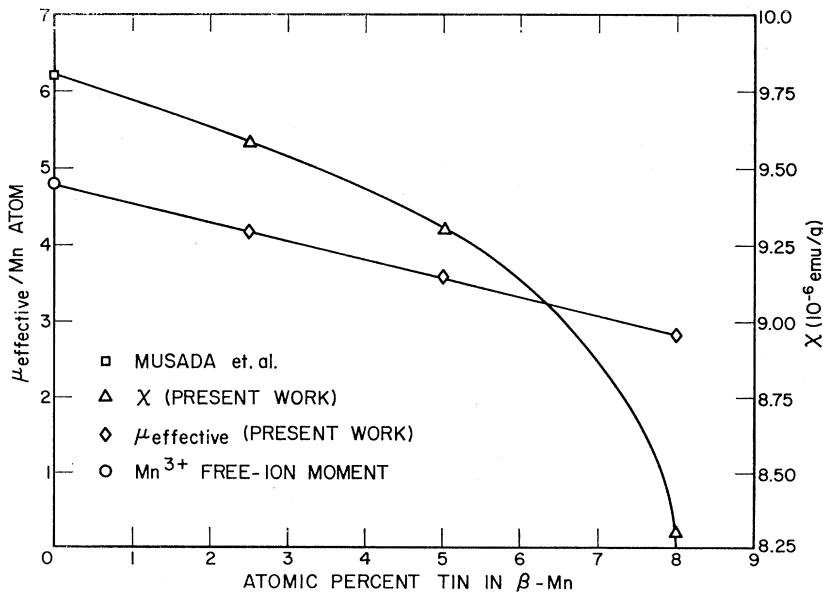


FIG. 2. Effective moment and room-temperature susceptibility as a function of tin concentration in  $\beta$ -Mn+Sn alloys.

<sup>6</sup> L. E. Drain, Proc. Phys. Soc. (London) **88**, 111 (1966).

<sup>7</sup> S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, Phys. Rev. **159**, 239 (1967).

<sup>8</sup> H. S. Moller and R. L. Mössbauer, Phys. Letters **24A**, 416 (1967).

TABLE II. Isomer shift and quadrupole splitting of  $\text{Sn}^{119}$  in  $\beta$ -Mn at 300°K relative to a  $\text{BaSn}^*O_3$  source at 300°K.  
The relative occupation of crystal sites is also given.

at.% Sn	Isomer shift (mm/sec)		Quadrupole splitting (mm/sec)		Relative occupation type-I/type-II sites
	Type I	Type II	I	II	
2.5	+2.02±0.02	+1.70±0.02	1.63±0.03	1.85±0.03	0.27
5.0	+2.00	+1.71	1.45	1.79	0.22
8.0	+2.03	+1.71	1.33	1.86	0.18

with a concomitant decrease in the relative occupation by Sn atoms of type-I sites; the change in splitting may be due to geometrical effects only.

The susceptibility at 300°K and the effective magnetic moment per Mn atom as a function of tin concentration are shown in Fig. 2. The effective moment is obtained from a plot of  $1/\chi$  versus  $T$  for temperatures between 80 and 300°K; the temperature dependence is very slight. The value of the effective moment per Mn atom undergoes a rather large change from  $4.2 \mu_B$  at 2.5-at.% tin to  $2.8 \mu_B$  at 8.0-at.% tin; the  $\text{Mn}^{3+}$  moment, which lies on the extrapolated curve of  $\rho_{\text{eff}}$  versus tin concentration, is  $4.8 \mu_B$ . The room-temperature susceptibility for the alloys decreases with an increase in tin concentration and the value extrapolated to pure  $\beta$ -Mn is in agreement with the determination of Musada *et al.*<sup>9</sup> Evidently there are changes in the character or occupation of the band structure that are not reflected at the Sn atoms.

<sup>9</sup> Y. Musada, K. Asayama, S. Kobayashi, and J. Itoh, *J. Phys. Soc. Japan* **19**, 460 (1964).

In conclusion, the isomer shift for Sn in  $\beta$ -Mn falls near to that of  $\text{Sn}^{119}$  in transition metals and  $\text{Sn}^{119}$  in  $\alpha$ -Sn.<sup>10</sup> Neither the isomer shift nor the quadrupole splitting reflects the concentration dependence shown by the magnetic susceptibility measurements; hence, any change in the electronic structure of the alloy which leads to phase instability must occur principally for Mn atoms. In addition, the large volume change with tin concentration does not affect the isomer shift at either site. There is a strong preference of the Sn atoms for the larger site (type II).

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<sup>10</sup> M. Cordey Hayes, in *Chemical Applications of Mössbauer Spectroscopy*, edited by V. I. Goldanski and R. H. Herber (Academic, New York, 1968), p. 314.