Temperature features of the magnetic interactions in manganese stannide

V. A. Virchenko and T. M. Tkachenko

Institute of Solid State and Semiconductor Physics of the National Academy of Sciences of

*Belarus, ul. P. Brovki 17, Minsk 220072, Belarus**

M. F. Thomas

Department of Physics, Oliver Lodge Laboratory, the University of Liverpool, England

Abstract

The features of the magnetic interactions in manganese stannide $Mn_{1.66}Fe_{0.02}Sn$ with a structure of the $B8_2$ type are investigated on the basis of Mössbauer-effect measurements on the iron and tin atoms. The Curie temperature of this compound according to the ^{57}Fe data is $T_C = 265$ K, while for ^{119}Sn it is $T_C = 250$ K; both of these are higher than the value of T_C determined by the Faraday method (240 K). The participation of the tin atoms in the magnetic exchange interaction in MnII–Sn–MnII chains is confirmed. It is shown that effectively only three of the five manganese atoms occupying the trigonal–bipyramidal MnII positions nearest to a tin atom have

*E-mail: lttt@ifttp.bas-net.by

any influence on the magnetic interactions at the tin nucleus. The magnetic fields at the nuclei of the manganese atoms in the trigonal–bipyramidal positions in MnII–Sn–MnII chains are significantly (2–2.5 times) larger than the field at the nuclei of the manganese atoms in the octahedral positions in MnI–MnI. KEYWORDS: Mössbauer effect, manganese stannide, magnetic exchange interaction

I. STATEMENT OF THE PROBLEM

Manganese stannide crystallizes in the $B8_2$ structure and is a phase of extended composition with a homogeneity region from 33 to 40 at.% tin.[1,2] Hexagonal close-packed tin atoms comprise the skeleton of the structure, the octahedral and trigonal–bipyramidal interstitial sites of which are occupied by manganese atoms (MnI and MnII). According to the magnetic properties, it is a ferromagnet[3–5] with an antiparallel (in the basal plane) orientation of the magnetic moments of the manganese atoms found in structurally inequivalent positions. The ability of manganese stannide to undergo a transition to a spin-glass state at temperatures below 100 K was noted in Refs. 6–8. The published data on the values of the magnetic moments of the atoms and the Curie temperatures are contradictory. For example, according to the results of Ref. 3, the temperature T_C falls from 269 to 256 K with increasing manganese content from $Mn_{1.5}Sn$ to $Mn_{1.8}Sn$, while according to Ref. 4 the decrease is from 263 to 226 K; according to Ref. 6 the transition temperature of $Mn_{1.74}Sn$ is $T_C \approx 230$ K, while in Mn_7Sn_4, according to Ref. 8, $T_C = 220$ K. Magnetic measurements[3] have given values of the magnetic moments per manganese atom of $3.5\mu_B$ in the octahedral and $2.2\mu_B$ in the trigonal–bipyramidal positions, while according to neutron-diffraction studies[5,6] they have the values $(0.8 \pm 0.2)\mu_B$ and $(3.8 \pm 0.2)\mu_B$. It is assumed that, as in Heusler alloys,[9] the magnetic interaction in manganese stannide[6] takes place in linear chains MnI–MnI–MnI and MnII–Sn–MnII (along the c axis).

The aforementioned discrepancies in the data demonstrate the need for additional studies

of the magnetic interactions in manganese antimonide. The goal of this study was to investigate the magnetic interactions in manganese stannide by the highly sensitive Mössbauer-effect method on two isotopes, ^{57}Fe and ^{119}Sn, and the change of their character when the temperature is lowered from room temperature ($T = 290$ K) to liquid-helium temperature ($T = 10$ K).

A feature of this investigation is that temperature studies of the Mössbauer effect are carried out simultaneously on the nuclei of atoms of (1) the cation sublattice (impurity iron atoms) and on the nuclei of atoms (2) of the anion sublattice (tin), which are a major consituent of the compound. Such studies permit comparison of the magnetic hyperfine interactions in the two kinds of atoms.

II. EXPERIMENT

A manganese stannide sample of composition $Mn_{1.66}Fe_{0.02}Sn$ is obtained by the known technology of melting the components, taken in the required portions by weight, in a quartz ampoule at $T = 1323$ K, with a subsequent anneal at $T = 1113$ K for 120 hours.[4] Instead of 2 at.% manganese, iron enriched in the isotope ^{57}Fe was introduced into the sample during the synthesis. The natural mixture of tin used in synthesizing the stannide was likewise enriched in the resonant isotope ^{119}Sn.

According to the results of x-ray diffraction studies, the lattice parameters of the $Mn_{1.66}Fe_{0.02}Sn$ sample investigated are $a = 0.438$ nm, $c = 0.550$ nm. According to magnetization studies by the Faraday method in a field of 0.86 T and in the temperature interval 80–300 K the magnetic characteristics of the sample are as follows: mean magnetic moment $\mu = 1.78\mu_B$ ($T = 80$ K), Curie temperature $T_C = 240$ K.

Mössbauer studies of the sample on the resonant ^{57}Fe atoms of $Mn_{1.66}Fe_{0.02}Sn$ were carried out in the temperature interval 10–300 K, and on ^{119}Sn in the interval 77–300 K. The measurements were made in the usual transmission geometry in the regime of constant accelerations, the sources of the resonant gamma rays were ^{57m}Co(Rh) and Ca^{119m}SnO$_3$, and

the isomer shifts were calculated relative to α-Fe and $CaSnO_3$.

III. RESULTS OF MÖSSBAUER STUDIES ON THE ISOTOPE ^{119}Sn

The results of temperature studies of the Mössbauer effect for ^{119}Sn in $Mn_{1.66}Fe_{0.02}Sn$ are presented in Fig. 1. The spectra were processed using the FfitA and FCFCORE_3 codes.[10] The subspectrum parameters obtained as a result of the processing of the ^{119}Sn spectra are presented in Table I: the isomer shifts (IS, mm/s), the quadrupole splittings (QS, mm/s), hyperfine magnetic fields at the tin nuclei (H_{eff}, T), and the areas of the subspectra (A_i).

The spectrum of manganese stannide on ^{119}Sn at room temperature is a quadrupole-split line and is processed in the model of an isolated doublet, which accords both with the structural features and with the nonmagnetic state of the compound.

As the temperature is lowered, the spectrum on tin transforms to magnetically split. The isotope shifts of the subspectra on the whole vary slowly with temperature. The slight displacement of the spectrum can be attributed to a temperature shift.[11] At $T = 250$ K, against the background of a persistent paramagnetic component, a magnetic interaction arises at the ^{119}Sn nuclei; this is at least 10 K higher than that determined by the Faraday method. With further decrease in temperature the hyperfine magnetic interactions and the corresponding fields at the ^{119}Sn nuclei grow in value all the way down to the lowest observation temperature $T = 77$ K. The field at the Sn nucleus determined in Ref. 12 for Mn_2Sn at $T = 80$ K was 190 kOe. We have found that between 250 and 120 K there are at least two different magnetic fields at the tin nuclei, but here the lines of the corresponding subspectra are broadened relative to the linewidth of the standard absorber. In the interval 120–77 K one observes three different values of the hyperfine magnetic fields at the ^{119}Sn nuclei. The broadening of the lines is indicative primarily of additional unresolved magnetic interactions which are hard to identify because of the overlap of the lines of the subspectra. Anomalous broadening is observed in the Mössbauer spectra taken in the region of the phase transition temperatures. Possible causes of the broadening besides an unresolved magnetic interaction

may be growth of the electric field gradient with decreasing temperature, noncoincidence of the directions of the gradients of the electric and magnetic fields at the nucleus,[13,14] and growth of the linewidth of tin with decreasing temperature.

In manganese stannide, which has the $B8_2$ structure (Fig. 2), the local environment of the tin atom has six octahedral positions MeI, which are assumed to be completely occupied by manganese atoms, and also five nearest trigonal–bipyramidal positions MeII. In our case in $Mn_{1-x}Sn$ with $x = 0.68$ these positions are partially filled with manganese atoms. Knowing the latttice parameters of the given sample ($a = 0.438$ nm, $c = 0.550$ nm), determined by x-ray diffraction, and the lattice angles, we calculated the distances from the tin to the nearest mangnese atoms MeI and MeII. The interatomic distances are presented in Table II. It is seen that three of the five MeII manganese atoms lie closer to the tin atom than the other two MeII atoms and the six MeI atoms. Since the magnetic interactions and electric quadrupole interactions are of a short-ranged character, the field at the tin nucleus is determined by the occupancy of the three nearest trigonal–bipyramidal MeII positions by manganese atoms. The features of the magnetic field created at the tin nucleus are reflected in the Mössbauer spectrum in the form of the subspectra. According to our assumption, four subspectra should be observed in the spectrum. The complete absence of manganese atoms in the three nearest of the five MeII positions gives a magnetically unsplit subspectrum. One manganese atom produces a small magnetic field at the tin nucleus, and this is manifested in a subspectrum with minimal magnetic splitting; two atoms create a field with a large magnetic splitting, and occupancy of the three nearest of the five MeII positions by manganese atoms gives a subspectrum with the maximum magnetic splitting in the tin spectrum.

The distribution of metal atoms over the trigonal–bipyramidal positions of the $B8_2$ structure is assumed to be random and described by a binomial law. In the present case of $Mn_{1+x}Sn$ with $x = 0.68$ the probability of filling of n of the five possible trigonal–bipyramidal positions[15] is given by the formula

$$\tag{1}$$

The occupation probabilities of the trigonal–bipyramidal positions calculated according to Eq. (1) are presented in Table III. Above, in accordance with the results of a calculation of the interatomic distances, we assumed that the contribution to the magnetic field at the tin nucleus from the three nearest MnII atoms is decisive, i.e., we are interested in the case $n = 0, 1, 2, 3$. At $T = 120$ and 77 K the tin spectra are modeled by three magnetic subspectra and one nonmagnetic, in complete agreement with the hypothesis that the spectrum is determined by the occupation of three of the five nearest MeII positions. Of the three nearest trigonal–bipyramidal positions, manganese atoms can occupy all three, only two, only one, or none (the magnetically unsplit subspectrum). The listed probabilities of filling of 0, 1, 2, or 3 positions at $T = 77$ K are in good agreement with the listed values of the areas of the respective subspectra (see Table III). This result confirms the known assumption that the tin atoms participate in exchange interactions in MnII–Sn–MnII chains, but it also shows that each tin atom interacts with the three nearest of the five possible manganese atoms in trigonal–bipyramidal MnII positions. The other two of the five MnII atoms lie 0.22 Å farther away from the tin atom; this is apparently a sufficient basis for substantial weakening of the magnetic interaction.

IV. RESULTS OF MÖSSBAUER STUDIES ON THE ISOTOPE ^{57}Fe

The initial spectrum on ^{57}Fe at temperature $T = 290$ K is a superposition of two sub-spectra in the form of doublets of different intensity (Fig. 3, Table IV), which correspond to metal atoms in two structurally inequivalent positions MeI and MeII and are indicative of the paramagnetic state of the metal atoms in both positions at the given temperature. The lines in the subspectra are slightly broadened relative to the linewidth of the Fe standard absorber ($\Gamma_{st} = 0.32$ mm/s). The isomer shifts of both subspectra practically coincide, so that one can assume that the electronic configurations of the iron atoms in the octahedral and trigonal–bipyramidal positions are identical and, according to the value of the isotope shift, correspond to the trivalent state of iron, Fe^{3+} (Ref. 14). The quadrupole splittings of

the subspectra are different, reflecting the different symmetry of the local environment of the metal atoms in the MeI (octa) and MeII (tetra) positions.

As the temperature is lowered, the values of the isotope shifts at the iron atoms increase. The centroid of the ^{57}Fe spectrum shifts from 0.44 to 1.12 mm/s as T is decreased from 290 to 10 K. Anomalous changes in the values of the isotope shifts, quadrupole splittings, and integral probability of the Mössbauer effect, analogous to those studied by us, have been observed, e.g., at the transition of substances to the superconducting state in connection with the washout of the electron density.[16,17] The value of the isomer shift is proportional to the electron density at the nucleus. Positive growth of the isotope shift at the iron atom as the temperature is lowered may mean an increase in the covalency of the chemical bond (i.e., a transition from the Fe^{3+} to the Fe^{2+} state), accompanied by the liberation of some of the electrons.

Against the background of the persistent paramagnetic components, a weakly expressed magnetic interaction at the ^{57}Fe iron nuclei appears at $T = 265$ K. The magnetic interaction at ^{119}Sn, as we have said, appears at $T = 250$ K, i.e., with a temperature lag of $\sim$15 K. With decreasing temperature the paramagnetic components vanish and the hyperfine magnetic interactions and the corresponding fields at the ^{57}Fe atoms grow in magnitude to the lowest observation temperature $T = 10$ K.

The low-temperature spectra of ^{57}Fe can be provisionally divided into two groups of subspectra with fields that differ substantially (by 2.5–3 times) from each other. The lines of the subspectra are broadened relative to the line of the standard absorber. The subspectrum with the higher value of the field clearly is that due to the manganese atoms in the trigonal–bipyramidal positions MeII. The value of the field at the iron nuclei in the trigonal–bipyramidal interstitial sites corresponds to the fields arising at the tin nuclei with a temperature lag of $\sim$15 K. The lower values of the field obviously correspond to manganese atoms which are found in the octahedral positions and interact with each other: MnI–MnI. These magnetic interactions are manifested at lower temperatures (starting from 200 K), although their integrated contribution is around 9/10. The probable reasons for such a rela-

tion between contributions from the atoms of the two sublattices are, first, the overall ratio of atoms in sublattices is 1 to 0.68, and second, according to the model proposed above on the basis of Mössbauer studies of the sublattice of tin atoms, only 3/5 of the manganese atoms in the MeII positions participate perceptibly in the magnetic interactions. Multiplication of the ideal concentration of 0.68 by the fraction of atoms participating in the interactions (0.6) gives a ratio of the subspectra of atoms in the MeI and MeII positions of 10 to 4. If it is taken into account that the trigonal–bipyramidal sublattice usually contains defects, while the octahedral sublattice is usually stably filled by metal atoms, we approach the real relationship of the contributions of the substrates to the spectrum.

The maximum effect magnetic fields can be evaluated accurately from the spectrum parameters. At $T = 50$ K the maximum field at the iron nucleus is 2.40 T, and, using the known[13,14] empirical formula $H_{\text{eff}} = a\mu_{\text{Fe}} + b\mu_1$, one can obtain a rough estimate of the corresponding magnetic moment of the iron atom. The empirical coefficients are: $a = 1.42 T/\mu_B$, $b = 0.14 T/\mu_B$. Since a is an order of magnitude larger, the second term of the formula is usually neglected in estimations. The value obtained for the magnetic moment of the iron atom is $\bar{\mu}_{\text{Fe}} = 1.69\mu_B$, which practically agrees with the value of $\bar{\mu}_{\text{Fe}}$ determined by the Faraday method at $T = 80$ K.

Taking into account the changes in the values of the IS and QS and the line broadening and its possible causes, we can consider it to be an experimentally established fact that at temperatures below 120 K differnt values of the magnetic field exist at both the iron and tin nuclei; the experimental spectra for both the iron and tin are modeled by at least three magnetic subspectra. The values of the maximum effective magnetic fields at the iron and tin nuclei at the same temperature are somewhat different. The maximum magnetic field at the ^{119}Sn nuclei at $T = 77$ K amounts to $H_{\text{eff}}^{\text{max}} = 2.16$ T, which is approximately 0.1–0.2 T lower than the fields at the iron at the same temperature. The field at the tin reaches the values at the iron with a small temperature lag. For example, at 240 K the fields at the iron nucleus is $H_{\text{eff}}^{\text{max}} = 1.03$ T, which is the same value that is reached at the tin nucleus at $T = 225$ K.

V. CONCLUSIONS

With decreasing temperature the magnetic interactions at the iron nuclei appear sooner than at the tin nuclei. The Curie temperature according to the Mössbauer data for ^{57}Fe in $Mn_{1.66}Fe_{0.02}Sn$ is $T_C = 265$ K, while according to the ^{119}Sn data $T_C = 250$ K (a lag of ~ 15 K); in both cases these are higher than the value measured by the Faraday method ($T_C = 240$ K). The maximum effective magnetic fields at the tin nuclei reach values equal to the fields at the iron nuclei, likewise with a temperature lag of ~ 15 K.

We have confirmed the participation of tin atoms in a magnetic exchange interaction in MnII–Sn–MnII chains. We have shown that effectively only three of the five manganese atoms occupying the trigonal–bipyramidal positions MnII influence the magnetic interactions at the tin nucleus.

The magnetic interactions of manganese atoms in the trigonal–bipyramidal positions in MnII–Sn–MnII chains are more intense than the interactions of manganese atoms in the octahedral positions, MnI–MnI, and the fields at the nuclei of the respective atoms differ by a factor of 2–2.5.

REFERENCES

[1] M. Elding-Ponten, L. Stenberg, A.-K. Larsson, S. Lidin, and K. Stahl, J. Solid State Chem. **129**, 231 (1997).

[2] M. Elding-Ponten, L. Stenberg, S. Lidin., G. Madariaga, and J.-M. Perez-Mato, Acta Cryst. B **53**, 364 (1997).

[3] Mitsuru Asanuma, J. Phys. Soc. Jpn. **17**, 300 (1962).

[4] Ko Yasukochi, Kazuo Kanematsu, and Tetuo Ohoyama, J. Phys. Soc. Jpn. **16**, 1123 (1961).

[5] N. S. Satya Murthy, R. J. Begum, B. S. Srinivasan, and M. R. L. N. Murthy, Phys. Lett. **15**, 225 (1965).

[6] R. Sugi, T. Shimomura, M. Matoba, S. Matsuzaka, S. Fujii, N. Hagiwara, and S. Anzai, Phys. Status Solidi B **189**, K65 (1995).

[7] N. Tokiwa, T. Yoshida, T. Shomomura, N. R. Sugi, M. Matoba, and S. Anzai, Phys. Status Solidi B **189**, K33 (1995).

[8] S. Anzai, F. Abe, Y. Takayama, S. Fujii, R. Sugi, A. Kakimoto, M. Narita, A. Kikuchi, and E. Mori, J. Magn. Magn. Mater. E **605**, 272 (2004).

[9] J. Kubler, A. R. Williams, and C. B. Sommers, Phys. Rev. B **28**, 1745 (1983).

[10] M. Attenborough, Ph. D. Thesis, University of Liverpool (1997).

[11] B. D. Josephson, Phys. Rev. Lett. **4**, 341 (1960).

[12] S. S. Hanna, L. Meyer-Schutzmeister, R. S. Preston, and D. H. Vincent, Phys. Rev. **120**, 2211 (1960).

[13] V. S. Shpinel', *Gamma-Ray Resonance in Crystals* [in Russian], Nauka, Moscow (1969).

[14] V. I. Gol'danskiĭ (ed.), *Chemical Applications of Mössbauer Spectroscopy* [in Russian], Mir,

Moscow (1970).

[15] E. A. Vasilev and T. M. Tkachenka, Crys. Res. Technol. **32**, 931 (1997).

[16] C. M. Lin and S. T. Lin., J. Phys.: Condens. Matter **5**, L247 (1993).

[17] N. P. Seregin, Fiz. Tverd. Tela (St. Petersburg) **45**, 12 (2003) [Phys. Solid State **45**, 11 (2003)].

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FIGURES

FIG. 1. Mössbauer spectra of manganese stannide on ^{119}Sn in the temperature interval 290–77 K.

FIG. 2. Structure of the $B8_2$ type.

FIG. 3. Mössbauer spectra of manganese stannide on ^{57}Fe in the temperature interval 290–77 K.

TABLES

TABLE I. Parameters of the Mössbauer spectrum of $Mn_{1.68}Sn$ on ^{119}Sn in the temperature interval 77–290 K.

KEY:

Number of subspectrum/parameters

IS, mm/s

QS, mm/s

H, T

TABLE II. Distance from the tin atom in $Mn_{1.66}Fe_{0.02}Sn$ to the nearest manganese atoms.

KEY:

No. of Mn atom

Position of Mn atom

Sn–Mn distance, Å

TABLE III. Probabilities of occupation of the trigonal–bipyramidal positions and relatively areas of the corresponding subspectra in the spectrum of $Mn_{1.66}Fe_{0.02}Sn$.

KEY:

No. of subspectrum

Number of filled MeII positions, n

Probability of filling n positions, P_n

Relative probability, $P_n / \sum P_n$

Area of the subspectrum in the experimental spectrum, A_n

Relative area, $A_n / \sum A_n$

TABLE IV. Calculated parameters of the Mössbauer spectra of $Mn_{1.66}Fe_{0.02}Sn$ on ^{57}Fe at $T = 10$–290 K.

KEY:

Number of subspectrum/parameters

IS, mm/s

QS, mm/s

H, kG