Systematics of hyperfine interactions at Sn and other $5s$-$5p$ diamagnetic impurities in ferromagnetic MnSb

G. S. Collins and N. Benczer-Koller
*Department of Physics, Rutgers University, New Brunswick, New Jersey 08903**

M. Pasternak
Department of Physics, Tel Aviv University, Ramat Aviv, Israel
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Mössbauer measurements on dilute ^{119}Sn impurities substituted for Sb in the ferromagnetic conductor MnSb were performed. The saturation hyperfine field at the tin site $H(0\ \mathrm{K}) = -90 \pm 1$ kOe was determined. The temperature dependence of the hyperfine field departs significantly from that of the bulk magnetization. The electric field gradient $eq = (15 \pm 4) \times 10^{17}\ \mathrm{V cm^{-2}}$ was measured and was found to be independent of temperature. The systematics of hyperfine fields at $5s$-$5p$ solutes in Fe, Co, Ni, and MnSb hosts are discussed.

INTRODUCTION

Over the last few years the transferred hyperfine interactions at diamagnetic solutes in magnetic hosts have been investigated by NMR and Mössbauer-effect techniques. These studies are important both for the elucidation of the mechanisms causing induced magnetic hyperfine interactions in diamagnetic atoms and for the understanding of the nature of the magnetism of the host proper.

No unique model yet exists which describes the magnitudes and signs of induced magnetic fields at the solutes, or their temperature dependence. As diamagnetic ions have no local moment, core polarization is negligible, and the magnetic hyperfine field arises from a very delicate interplay between contributions of similar magnitude but opposite sign, such as conduction-electron spin polarization, or the polarization resulting either from the overlap of the host magnetized shell with the solute valence electrons or from covalent bonding.

A series of diamagnetic impurities which has been used for studies of systematics of the internal magnetic fields (H_{hyp}) is the $5s$-$5p$ group, extending from Sn to Xe. Indeed many measurements have been carried out on those solutes in several transition metals and alloys. The results obtained for[1-3] Fe and[4-6] MnSb hosts, which at first sight are different types of ferromagnetic conductors, are of particular interest: the magnetic hyperfine fields at impurities of Sb, Te, and I in these two hosts are remarkably similar in both magnitude and sign.

In the present work we investigated the electric and magnetic hyperfine interactions at Sn impurities in MnSb by use of the Mössbauer effect on ^{119}Sn. Both the magnitude and the sign of H_{hyp} and the electric field gradient (EFG) were obtained as a function of temperature.

EXPERIMENTAL

A. Sample preparation and measurements

The MnSb (^{119}Sn) absorber was prepared by heating elemental Mn (100 mg), Sb (205 mg), and enriched ^{119}Sn (1.95 mg) in an evacuated quartz amoule at 600 °C for 72 h. The atomic composition $Mn_{1.068}Sb_{0.990}{}^{119}Sn_{0.010}$ falls within the range of homogeneity of the NiAs structure in the ternary Mn-Sb-Sn phase diagram.[7] The ^{119}Sn impurity lies substitutional on the Sb site. The material was quenched in water at room temperature. An absorber was prepared by thoroughly grinding the material with Al_2O_3 powder and encapsulating the mixture. Initial spectra were broad; sharp spectra were obtained after annealing the material at 450 °C for 16 h and cooling gradually to room temperature. The measurements were made with a V-Sn alloy Mössbauer source[8] at room temperature. The isomer shift δ of V-Sn with respect to a $BaSnO_3$ source is $+1.57$ mm sec^{-1} at room temperature.

At low-absorber temperatures a well-resolved spectrum was observed, consisting of the six-line Zeeman spectrum and an additional single impurity line probably corresponding to tin metal precipitate. Figure 1 shows the spectra obtained at 77, 298, and 387 K as well as the data at room temperature in the presence of a 4.4-kG transverse external magnetic field.

B. Spectral analysis

The spectra were fitted to the impurity line and to the six lines resulting from the splitting of the ground $I = \frac{1}{2}$ and excited $I^* = \frac{3}{2}$ nuclear states under

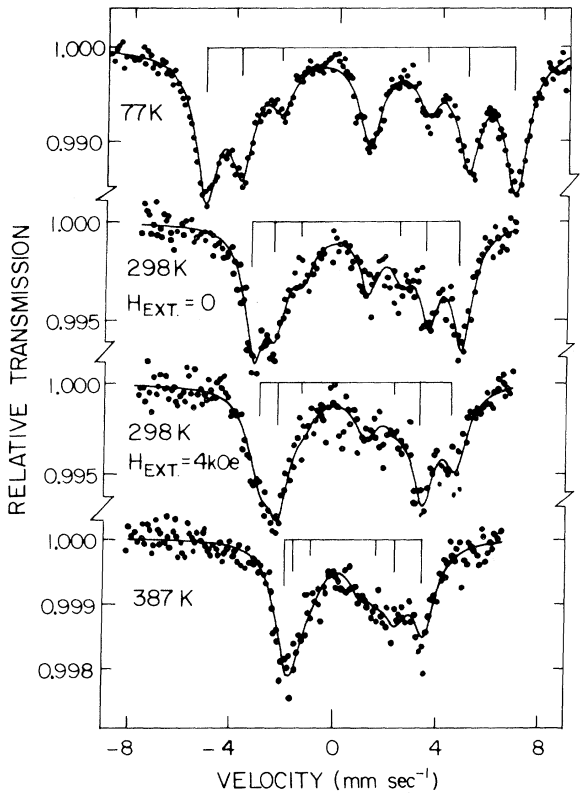

FIG. 1. Mössbauer spectra of ^{119}Sn substituted for Sb in $Mn_{1.068}Sb$. A comparison of the middle two spectra shows that upon application of an external magnetic field, H_{hyp} decreases at the ^{119}Sn site. The peak near 1 mm sec^{-1} is an impurity line.

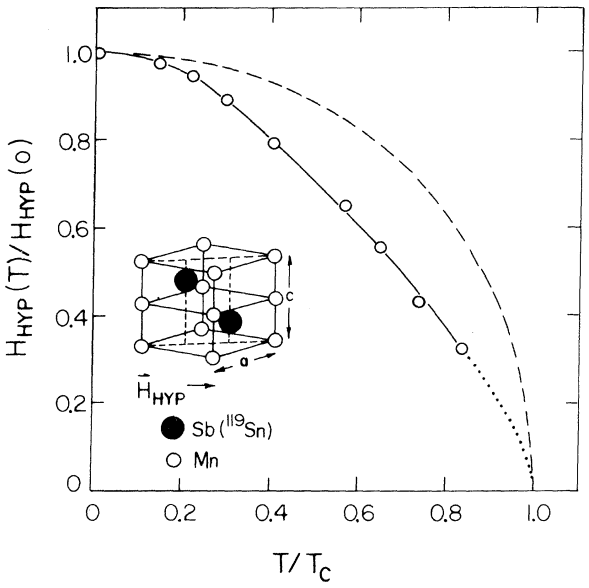

FIG. 2. Temperature dependence of H_{hyp} at ^{119}Sn substituted for Sb in $Mn_{1.068}Sb$. The dependence of the bulk magnetization $M(T)/M(0)$ is also shown (dashed line). The diagram of the unit cell shows the Sb(^{119}Sn) sites at the centers of trigonal bipyramids of Mn atoms.

the influence of combined magnetic dipole and electric quadrupole interactions:

$$E_m = -m\mu H_{hyp}/I$$

and

$$E_m^* = -\frac{m\mu^* H_{hyp}}{I^*} + \frac{(-1)^{|m|+1/2} e^2 Q^* q}{4} \frac{3\cos^2\theta - 1}{2},$$

where θ is the angle between the internal magnetic field H_{hyp} and the principal axis (c axis) of the axially symmetric EFG tensor. The values[9] of the nuclear moments used in the fitting and analysis were $\mu = -1.0462$ nm, $\mu^* = 0.685(3)$ nm, and $Q^* = -0.06(2)b$.

RESULTS

From the contraction of the Mössbauer spectrum upon application of the external magnetic field, the internal field is seen to be *negative*.

The temperature dependence of the internal field is displayed in Fig. 2, where the microscopic magnetization at the Sn nuclei normalized to the value at 0 K is compared to the normalized curve of the bulk magnetization[10] for the composition of our sample. The temperature dependence of H_{hyp} is seen to deviate significantly from that of the host magnetization. $H_{hyp}(0\ K) = -90.3(1.0)$ kOe was extrapolated from the low-temperature experimental points. The high-temperature data indicate a Curie temperature $T_C = 525$ K consistent with that deduced from the magnetization measurements[10-13] on $Mn_{1+x}Sb$ samples.

An electric field gradient $eq = +(15 \pm 4) \times 10^{17}$ V cm^{-2} independent of temperature was observed. These results were evaluated for an angle $\theta = 90°$ between the EFG axis and H_{hyp} as determined by neutron-diffraction measurements.[7]

The characteristic Debye-Waller temperature $\Theta_{DW} = 168$ K was derived from the relative areas of the high-temperature Mössbauer spectra. The experimental results are summarized in Table I.

DISCUSSION: SYSTEMATICS OF THE HYPERFINE INTERACTIONS IN THE 5*s*-5*p* SOLUTES

MnSb is a metallic ferromagnetic compound with the NiAs($B8$) structure. Its ferromagnetic and electrical properties have been extensively investigated.[7,10-13] From those studies the following pertinent conclusions were derived. MnSb is a metal with hole conductivity with its Fermi level in the 5s-5p bonding band. The antibonding band is empty and lies just above the Fermi level, consequently

TABLE I. Summary of experimental results obtained from Mössbauer spectra. ^{119}Sn in $Mn_{1.068}Sb$.

H_{hyp}(°K) (kOe)	$\frac{e^2qQ^*}{4}\frac{3\cos^2\theta-1}{2}$ (mm sec^{-1})	eq for $\theta=90°$ (10^{17} V cm^{-2})	$\delta_{V\text{-}Sn}$(298 K) (mm sec^{-1})	T_c (K)	Θ_{DW} (K)
−90.3(1.0)	+0.135(10)	+14.6(4.4)	+0.45(4)	525	168

leaving some holes in the $5s$-$5p$ band. It is expected that the special features of this magnetic conductor play a role in the conduction-electron polarization mechanism different from that observed in transition metal hosts.

Figure 3 shows the dependence of H_{hyp} at Sn, Sb, Te, and I solutes in MnSb and in Fe, Co, and Ni hosts, as well as the systematics of the EFG for the same solutes in MnSb.[14]

Some features from Figs. 2 and 3 must be emphasized. The magnitudes of the hyperfine fields at the $5s$-$5p$ solutes in the Fe and MnSb hosts are almost equal and the signs are the same; however, the host-ion magnetic moments are very different, $3.55\mu_B$ and $2.2\mu_B$ for MnSb and Fe, respectively.[7] Furthermore, while the internal field at Sn in Fe and in Ni (Ref. 15) follows closely the temperature dependence of the bulk magnetization, and is explained well by a molecular-field theory, the temperature dependence of the hyperfine field departs dramatically from the magnetization in the case of the Co (Refs. 16, 17) and MnSb hosts. A similar behavior has been observed[18] at ^{119}Sn in the intermetallic compound FeSn.

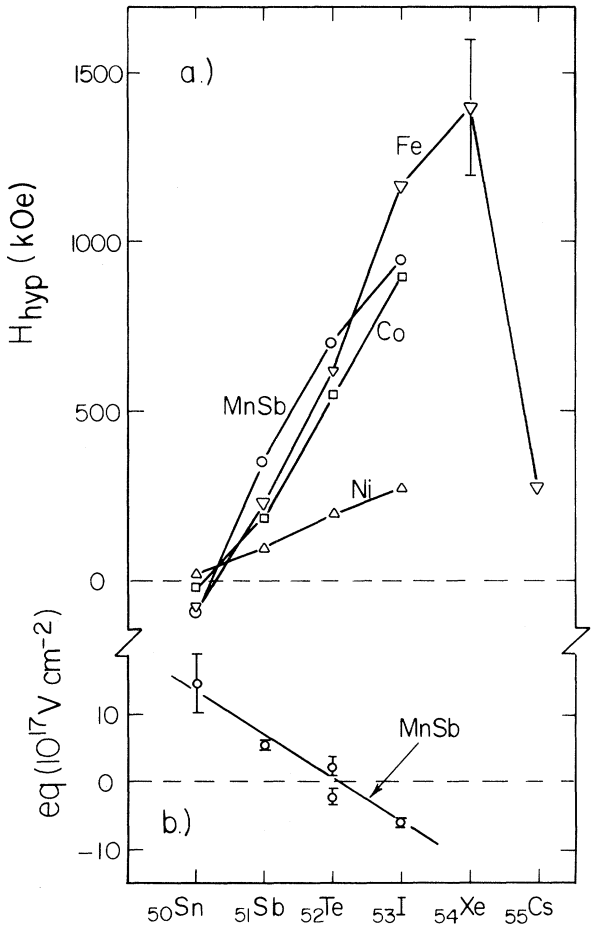

FIG. 3. (a) Systematics of H_{hyp} at solutes in the $5sp$ electronic series in a number of ferromagnetic hosts. (b) Systematics of the EFG at $5sp$ solutes in MnSb. The sign of the quadrupole interaction at Te is not determined.

The change in sign of H_{hyp} between Sn and Sb and the positive values of H_{hyp} for the higher Z solutes have stimulated several views concerning the origin of the induced hyperfine interactions wherein contributions of opposite sign compete sensitively with each other.

Conduction-electron spin polarization arises from RKKY indirect exchange interactions between the magnetic ions and the conduction electrons, and in general contribute a negative term to the hyperfine field[19,20] $s-d$ interband mixing and hybridization may occur and would also contribute a negative hyperfine field[21]; charge perturbation[22] due to the scattering of exchange polarized conduction electrons by the impurity atom has been shown to yield large positive hyperfine fields for high Z impurities. These contributions are all expected to scale with the moment of the host. In addition, large positive contributions to H_{hyp} may arise from direct overlap[23] of a polarized orbital of the magnetic atom and bound s-type orbitals of the nonmagnetic atom. Overlap effects ought also to be proportional to the moment of the host as well as to the degree of volume overlap between the solute and the neighboring magnetic host ions. For the cases of Fe, Co, and Ni hosts, both these expectations are qualitatively satisfied. However, in the case of MnSb, the magnitude of the induced field does not scale with the host moment. In addition, whereas Te and I impurities occupy somewhat larger volumes than the Sb they replace, Sn occupies much less than the available volume.[24] It is therefore quite surprising that not only the magnitude but the dependence of the hyperfine field on Z remain the same in MnSb as in the Fe host. In gen-

eral, models based on the various contributions described above explain the data only qualitatively and only for particular combinations of impurity and host.

The anomalous behavior of $H_{hyp}(T)$ at ^{119}Sn in Co has been qualitatively explained[17] by assuming that the Sn atom and some fraction of its nearest neighbors (the fraction depending on concentration) respond with temperature as a spin polarized unit, for which the exchange coupling with the host metal is different from the host-host coupling. However, the possibility of a particular exchange coupling between Sn and its nearest Co neighbors that is different from the exchange coupling in the host has been ruled out by an experiment,[25] which showed that $H_{hyp}(T)$ at the Co nuclei which are first nearest neighbors to Sn in a Co(2-at.% Sn) alloy does not deviate significantly from the Co bulk metal hyperfine field. Undoubtedly both in MnSb and in Co hosts different mechanisms must be operating.

Another interesting feature concerns the dependence of the EFG on Z. From crystallographic considerations the principal axis of the EFG is along the hexagonal c axis, perpendicular to the direction of the magnetization. As can be seen from Fig. 2, the EFG varies linearly from Sn to I, changing sign near $Z = 52$ (Te). This occurrence suggests a redistribution in the local charge distribution about the impurity. Whereas in the case of ionic I^- the negative EFG is due to an excess of p electrons in the z direction, in the case of Sn the positive EFG may well be due to an excess of p holes in the Sn-Mn directions, corresponding to the promotion of p electrons from the Sn atom to the Sn-Mn bond.

It is noteworthy that no phase transition in which the angle θ changes from 90° to 0° was detected in the temperature range studied here. This effect has been reported[11] to occur in pure MnSb at 520 K.

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[24]From the isomer shift-data it is inferred that the electronic state of Sn lies between that of β-Sn ($\delta = 2.56$ mm sec^{-1} relative to $BaSnO_3$) and α-Sn ($\delta = 2.05$ mm sec^{-1} relative to $BaSnO_3$), namely, very close to atomic Sn which has an atomic radius of about 1.45 Å. This value is considerably smaller than that of the Sb^{3+} cation in MnSb. From crystallographic data [*Handbook of Chemistry and Physics*, 53rd ed., edited by R. C. Weast (Chemical Rubber Co., Cleveland, 1972), p. E-57] the Mn-Sb distance was evaluated to be 2.79 Å and since the ionic state of Mn is between 2^+ and 3^+ ($r = 0.80$ and 0.66 Å, respectively) an approximate value of the ionic radius of Sb of 2.05 Å is obtained. Thus the Sn solute is rather "loosely" bound to its neighbors, resulting in reduced overlap between its 5s outer shell and the 3d shells of the Mn ions. Similarly, the δ for ^{125}Te and ^{129}I in MnSb correspond to $^{-1}$I and $^{-2}$Te ionic states with radii of 2.1 and 2.2 Å, respectively, progressively larger than that of the available volume.
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