Temperature dependence and anisotropy of the hyperfine interaction for ^{119}Sn impurity atoms in ferrimagnetic Mn_2Sb

N. N. Delyagin, V. I. Nesterov, and A. K. Churakov

Institute of Nuclear Physics, M. V. Lomonosov State University, Moscow

(Submitted 1 April 1987)
Zh. Eksp. Teor. Fiz. **93**, 1480–1486 (October 1987)

Mössbauer spectroscopy is used to measure the temperature dependence of the magnetic hyperfine field (B) for ^{119}Sn impurity atoms in ferrimagnetic Mn_2Sb. The unusual shape of this dependence is due to two competing contributions of opposite signs and to the large anisotropy of the hyperfine interaction. The contributions to B from the two magnetic sublattices are determined, together with the isotropic and anisotropic components of B. The dependence of the electron polarization on the angle θ between the magnetic moments of the Mn atoms and the direction of the Sn—Mn bond is considered. The angular dependence of the anisotropic component of B suggests a pseudodipole origin for the anisotropic exchange between the magnetic electrons of the Mn atoms and the valence electrons of Sn. The polarization for $\theta = 0°$ is almost twice as large as for $\theta = 90°$.

1. INTRODUCTION

Recent experimental data indicate that the magnetic hyperfine interaction for tin atoms in intermetallides may be highly anisotropic. As an example, we may cite the data for Sn impurity atoms in cubic Laves phases of the type RAl_2, where R denotes a rare-earth element.[1] In these phases, the magnetic hyperfine field is sensitive to the direction of the magnetic moments of the R-ions relative to the local axis of symmetry characterizing the spatial distribution of the electron density. The situation for the intermetallide $FeSn_2$ is of interest, because the interpretation suggested in Ref. 2 predicts that the magnetic hyperfine interaction for the Sn atoms should be completely anisotropic.

The angular dependence of the magnetic hyperfine interaction deserves careful study, because it reflects some important features of the mechanisms by which exchange occurs and the valence electrons of the nonmagnetic atom become polarized. The anisotropic component of the magnetic hyperfine interaction is conventionally attributed to the polarization of the valence p-electrons, whose wave function is not spherically symmetric. Such an approach is awkward for analyzing the situation in intermetallide compounds, because the valence electrons form hybrid orbitals in which the p-component can be identified only formally by a procedure that neglects the actual mechanisms for exchange polarization. Further difficulties arise from the fact that the Fermi contact interaction vanishes for p-electrons, yet it is always the primary (or even only) source for generating the hyperfine magnetic field for atoms with a zero intrinsic magnetic moment. One should in fact consider the anisotropic polarization of the complete electron density distribution whenever the latter is not spherically symmetric.

Mössbauer spectroscopy can be used to investigate the anisotropy of the magnetic hyperfine interaction without requiring the use of external magnetic fields and single crystals. Systems in which the alignment of the magnetic moments changes with temperature are particularly well-suited to this method. This approach makes it possible to observe the anisotropy without externally perturbing the system in any way. In our present work we investigated one such system, the ferrimagnetic compound Mn_2Sb, in which a few of the Sb atoms were replaced by ^{119}Sn.

All the Sb atoms are structurally equivalent in Mn_2Sb, which has the $C\,38$ tetragonal structure (of the same type as Cu_2Sb) and lattice constants $a = 0.408$ nm, $c = 0.656$ nm (Fig. 1). The Mn atoms occupy two inequivalent positions, MnI and MnII. The MnII atoms are nearly coplanar with the Sb atoms, while the MnI atoms occupy planes devoid of Sb atoms. Each Sb atom has 9 Mn neighbors: 4 MnI atoms at a distance of 0.275 nm, one MnII atom at 0.282 nm, and 4 MnII atoms at 0.289 nm. The Curie point for this collinear ferrimagnetic compound is $T_c = 550$–565 K (Refs. 3, 4). The MnI and MnII atoms comprise two magnetic sublattices with oppositely aligned magnetic moments. The atomic moments were measured by neutron diffraction in Refs. 4–6. According to Ref. 4, the magnetic moments of the MnI and MnII atoms (extrapolated to $T = 0$ K) are equal to $2.1\mu_B$ and $3.9\mu_B$, respectively. The direction of the resultant magnetization depends on the alignment of the magnetic moments in the MnII sublattice. It is important to note that the magnetic moments of the two sublattices depend differently on temperature: as T increases, the MnII moments decrease much faster than the MnI moments. The data in Ref. 4 indicate that at room temperature, the average moments for the

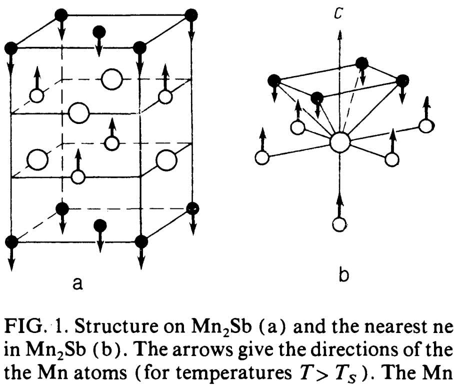

FIG. 1. Structure on Mn_2Sb (a) and the nearest neighbors of an Sn atom in Mn_2Sb (b). The arrows give the directions of the magnetic moments of the Mn atoms (for temperatures $T > T_S$). The MnI and MnII atoms are denoted by ● and ○; the large open circles without arrows denote Sb (or Sn impurity) atoms.

MnI and MnII atoms are 16 and 25% less than their values at 0 K, respectively. Information on the temperature dependence of the moments has also been obtained by NMR (Ref. 7). Unfortunately, the neutron diffraction data are not very accurate, while the NMR data were obtained only indirectly by parametrizing the temperature dependences of the magnetic hyperfine fields for the Mn atoms. Both sets of data will be used below to analyze our measurement results; the discrepancies in the data will not affect our principal conclusions.

The compound Mn_2Sb has a spin-flip transition, which in pure Mn_2Sb occurs at $T_S = 240–250$ K. The NMR data[7] indicate that the transition takes place within a temperature interval of width 5–6 K from 245 to 250 K. At low temperatures ($T < T_S$) the moments lie in the basis plane, while at high temperatures ($T > T_S$) they are aligned along the c-axis of the lattice. The magnitudes of the moments do not change during the spin flip. The magnetic properties of Mn_2Sb are extremely sensitive to impurities, which can greatly alter both T_C and T_S. A transition to an antiferromagnetic state has been observed in some cases.[3,5,8]

In Ref. 9, Mössbauer spectroscopy was employed to measure the magnetic hyperfine fields for ^{119}Sn in the compound $Mn_2Sb_{0.98}Sn_{0.02}$ at 80 and 300 K. The fields at these two temperatures differed considerably, which was attributed to the anisotropy of the magnetic hyperfine interaction. The temperature dependence of the hyperfine field was not measured in Ref. 9.

2. EXPERIMENTAL METHOD AND RESULTS

The measurements were made on several alloys of identical composition $Mn_2Sb_{0.997}Sb_{0.003}$ which were prepared by fusion in an induction oven in an argon atmosphere. The tin impurity was enriched to 92% in the isotope ^{119}Sn, and the alloys were remelted several times to ensure homogeneity. Several of the specimens were annealed at 700 K for 30 h; however, this had little effect on the Mössbauer spectra. The specimens contained a small amount (a few percent) of an extraneous phase of unknown composition which gave rise to weak lines near the center of the spectrum. This phase was included in our analysis of the spectra and did not significantly reduce the accuracy in determining the parameters of the primary spectrum.

The Mössbauer absorption spectra of ^{119}Sn were recorded using gamma-radiation at 23.9 keV by means of an electrodynamic spectrometer operating at constant acceleration with a $CaSnO_3$ source, maintained at room temperature. The temperature of the specimen ranged from 77 to 550 K, and during each measurement the temperature was kept constant to within 0.1 K. In the analysis the spectra were approximated as a sum of Lorentzian lines. The quadrupole shift in the components of the hyperfine structure was small enough to be treated by perturbation theory. The widths of the components of the hyperfine structure were less than 1 mm/s, which indicates that the specimens were highly ordered and that the parameters of the hyperfine interaction did not vary.

The magnetic hyperfine fields for the ^{119}Sn impurity atoms were found to be 9 (1) and 61.6 (5) kOe at 77 and 295 K, respectively. These values agree with the ones in Ref. 9 obtained for specimens with a higher concentration of tin impurity. Measurements in external magnetic fields carried out at 77 and 295 K revealed that the magnetic hyperfine field was positive, i.e., parallel to the magnetization vector of the MnII sublattice. The isomeric shift was equal to 1.98(3) mm/s at 77 K and 1.89(1) mm/s at 295 K. The quadrupole interaction constant e^2qQ was equal to $+ 0.428)$ mm/s and was essentially independent of temperature. The Curie temperature deduced from the temperature dependence of the hyperfine field was 543.5(5) K.

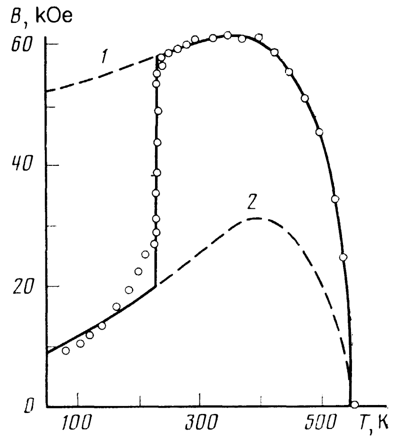

FIG. 2. Temperature dependence of the magnetic hyperfine field B for Sn impurity atoms in Mn_2Sb. The solid curve is calculated by Eq. (6). The dashed curves show the temperature dependence that would be observed if no spin-flip transition occurred. For curve 1 the moments of the Mn atoms are parallel to the c axis; for curve 2, they lie in the basis plane.

Figure 2 shows the measured temperature dependence of the magnetic hyperfine field $B(T)$. The form of the curve is unusual; at low temperatures ($T < T_S$) the hyperfine field increases with T, while for $T > T_S$ it remains virtually constant in the interval 240–400 K, even though the magnetization decreases greatly. The spin-flip transition is clearly accompanied by a marked change in the magnetic field; this indicates that the anisotropic component comprises a substantial fraction of the total hyperfine field. Our specimens satisfied $T_S \approx 230$ K, which is 15–20 K less than T_S for pure Mn_2Sb. The fact that T_S and T_C are below their nominal values for pure Mn_2Sb can only be due to the presence of the tin impurity. The random distribution of the impurity atoms caused a perceptible broadening of the spin-flip transition. For this reason (and also due to the smallness of the quadrupole shift), we were unable to investigate the rotation of the magnetic moments in detail near the transition.

In calculating the contribution from the magnetic dipole interaction to the observed local magnetic field, we carried out the dipole summations over the magnetic moments of Mn atoms located within 100 lattice constants from a given Sn atom. We found that the anisotropy of the dipole field (i.e., its change during the spin-flip transition) was equal to 1.5 kOe. This is small compared to the total change in the local field during the transition and will be neglected in the following analysis.

3. ANALYSIS OF THE RESULTS

The general behavior of the curve $B(T)$ shown in Fig. 2 leads immediately to some qualitative conclusions regarding the properties of the magnetic hyperfine interaction for Sn impurity atoms in Mn_2Sb. The magnetic hyperfine field is the sum of the contributions from the MnI and MnII sublattices; since the moments in these sublattices are oppositely directed, these contributions should be of opposite sign. The dependence $B(T)$ does not follow the temperature curves for the resultant magnetization nor for the magnetizations of the individual sublattices. Clearly, this is because the two sublattice contributions cancel partially, and also because the moments in the two sublattices have different temperature dependences, as discussed above. The increase in B with T for $T < T_S$ and the constancy of B over a wide temperature interval for $T > T_S$ indicate that the dominant contribution must come from the MnI sublattice, whose moments depend less strongly on temperature. Since the resultant field is positive, the contribution from the MnI sublattice must therefore be positive, while that from the MnII sublattice is negative (and smaller in absolute value). If we recall that the moments of the MnI atoms are antiparallel to the total magnetization, we see that both contributions are negative relative to the alignment of the moments that give rise to them. The dominant contribution from the MnI sublattice can be explained naturally in terms of the behavior of the contributions to the hyperfine field (because the distance Sn–MnI is much less than the distances Sn–MnII). Both of these conclusions accord completely with the general behavior observed for Sn atoms in magnetic materials based on the transition metals.[10] One finds that the interaction with the nearest magnetic neighbors always gives a negative contribution to the hyperfine field, and its absolute value decreases rapidly with increasing interatomic distances.

The temperature dependence of the magnetic hyperfine field for Sn atoms in Mn_2Sn can be expressed in the general form

$$B(T) = am_{\rm I}(T) + bm_{\rm II}(T), \tag{1}$$

where a and b are constants and $m(T) = M(T)/M(0)$ is the reduced magnetization of the corresponding sublattice, denoted by the subscripts I and II for MnI and MnII, respectively. The two contributions to the field are assumed to be additive and proportional to the respective magnetic moments. The coefficients a and b in (1) are constant only within the temprature intervals $T < T_S$ and $T > T_S$; they include both the isotropic and the anisotropic components of the hyperfine field. We will show below that the anisotropic components for the two contributions change differently during the spin-flip transition. Therefore, both the magnitudes of the contributions and their ratio change during the transition.

In the high-temperature region ($T > T_S$), the coefficients in Eq. (1) can be found directly by comparing (1) with experimental data. A least-squares analysis gives $a = 205$ kOe and $b = -153$ kOe. The error in determining these coefficients depends entirely on the error in the functions $m(T)$ and is $\sim 10\%$. With these coefficients, Eq. (1) accurately reproduces the experimental curve $B(T)$ for $T > T_S$. At low temperatures, both $m_{\rm I}(T)$ and $m_{\rm II}(t)$ are close to unity and neither is known well enough to permit a reliable determination of the coefficients in (1) by this method. Under suitable simplifying assumptions, a and b in (1) can be found throughout the temperature interval by analyzing the temperature dependence $B(T)$ together with the changes in the contributions to B during the spin-flip transition, and this procedure can also be used to find the isotropic and anisotropic components of the magnetic hyperfine field.

Indeed, let us assume that the magnetic hyperfine field for the Sn impurity in Mn_2Sb depends only on the nearest-neighbor Mn atoms. The contribution to the field from each Mn atom can then be expressed as

$$B_i = C + D\cos^2\theta, \tag{2}$$

where C and D are the isotropic and anisotropic components, respectively, and θ is the angle between the magnetic moment of the ith Mn atom and the direction of the Sn—Mn bond. If (as above) we regard the hyperfine field as the sum of the contributions from the two sublattices, the coefficients a, b in Eq. (1) can now be expressed in the form

$$a = C_{\rm I} + D_{\rm I}\langle\cos^2\theta\rangle_{\rm I}, \quad b = C_{\rm II} + D_{\rm II}\langle\cos^2\theta\rangle_{\rm II}, \tag{3}$$

where the parameters C and D correspond to the isotropic and anisotropic contributions from each sublattice, and $\langle\cos^2\theta\rangle$ is the average value of $\cos^2\theta$ for the Mn atoms in the sublattice. If we suppose further that the ratio C/D is the same for all of the Mn atoms, we can rewrite (3) as

$$a = C_{\rm I}(1 + \alpha\langle\cos^2\theta\rangle_{\rm I}), \quad b = C_{\rm II}(1 + \alpha\langle\cos^2\theta\rangle_{\rm II}), \tag{4}$$

where $\alpha = D_{\rm I}/C_{\rm I} = D_{\rm II}/C_{\rm II}$. The three parameters $C_{\rm I}$, $C_{\rm II}$, and α in (4) can be found by solving a system of three equations. The first two correspond to the values of a and b found above for $T > T_S$, while the third can be derived by analyzing how the hyperfine field changes during the spin-flip transition. The molecular structure data imply the following values for $\langle\cos^2\theta\rangle$ in the temperature intervals $T > T_S$ ($M \| c$) and $T < T_S$ ($M \perp c$): 0.45 and 0.28 for MnI, 0.2 and 0.4 for MnII. If we ignore the temperature dependence of the magnetic moments (i.e., consider the hypothetical case of a spin-flip transition near $T = 0$ K), the change in the hyperfine field during the transition is equal to

$$\Delta B = B(M\|c) - B(M\perp c) = \Delta B_{\rm I} + \Delta B_{\rm II} = 0.17C_{\rm I}\alpha - 0.2C_{\rm II}\alpha. \tag{5}$$

To find ΔB at room temperature, one must multiply the first and second terms in (5) by $m_{\rm I}(T)$ and $m_{\rm II}(T)$, respectively. Since $C_{\rm II}$ is negative, the signs of the contributions of the two magnetic sublattices to ΔB are the same.

Best agreement with experiment throughout the range of temperatures is obtained using the following values:

$$\alpha = 0.84, \quad C_{\rm I} = 150\ \text{kOe}, \quad D_{\rm I} = 124\ \text{kOe},$$

$$C_{\rm II} = -130\ \text{kOe}, \quad D_{\rm II} = -111\ \text{kOe}.$$

These values are accurate to within 10–15%; most of the error is due to the error in determining the functions $m(T)$. The temperature dependence of the magnetic hyperfine field for all T is thus given by

$$B(T) = (150 + 124\langle\cos^2\theta\rangle_{\rm I})m_{\rm I}(T) - (130 + 111\langle\cos^2\theta\rangle_{\rm II})m_{\rm II}(T). \tag{6}$$

The solid curve in Fig. 2 shows $B(T)$ calculated by this formula. On the whole, Eq. (6) agrees quite well with the experimental results. The small divergence for $T < T_S$ may be due to the broadening of the spin-flip transition, as well as to unreliability in $m(T)$ at low temperatures.

The result $\alpha = 0.84$ indicates that the magnetic hyperfine interaction for Sn atoms in Mn_2Sb is highly anisotropic: the polarization of the Sn valence electrons when $\theta = 0°$ is nearly twice as great as when $\theta = 90°$. The polarization is greatest when the inducing magnetic moment lies along the Sn—Mn bond. Such an angular dependence of the electron polarization may be expected whenever the anisotropic component of the exchange interaction is "pseudo-dipole" in character and the electron density distribution is concentrated along the Sn—Mn bonds. The effective exchange field, corresponding to the anisotropic component of the pseudodipole exchange between an Sn valence electron and a magnetic electron with spin **S**, is proportional to the vector

$$\mathbf{r}(\mathbf{S}\mathbf{r}), \tag{7}$$

where the radius vector **r** gives the relative position of the interacting electrons. In this case, the anisotropic polarization of the valence electron is clearly greatest when **S** and **r** are parallel (or antiparallel), and it is collinear with the vector **r**. If the electron density is distributed symmetrically about the Sn—Mn bond and elongated along it, the total polarization of the valence electrons will be greatest when the magnetic moment is parallel to the bond (i.e., when $\cos\theta = \pm 1$). We note that in general, the isotropic and anisotropic components of the magnetic hyperfine field need not be parallel (the former is collinear with **S**); noncollinearity of the vectors **B** and **S** has apparently been observed in antiferromagnetic $FeSn_2$ (Ref. 2). However, these components are collinear for Sn impurity atoms in Mn_2Sb, because the distribution of the magnetic atoms is axisymmetric. In this case, the projection of the vector (7) on **S** is significant for each bond. The anisotropic component of the polarization is consequently proportional to $\cos^2\theta$, in agreement with Eq. (2), which was used to analyze the experimental data.

The above relationship between the anisotropic polarization and the shape of the electron density distribution may turn out to hold quite generally for Sn atoms in alloys and intermetallides. A similar dependence of the hyperfine field on the alignment of the magnetic moments was noted for Sn impurity atoms in the intermetallides $GdAl_2$ (Ref. 1) and $TmFe_2$ (Ref. 11), where the Sn atoms substituted some of the Al and Fe atoms, respectively. In both cases, the polarization of the Sn valence electrons was greatest when the inducing magnetic moments were parallel to the axis of maximum valence electron density. The sign of the anisotropy of the magnetic hyperfine interaction for Sn atoms in metallic gadolinium and in dilute Gd-based alloys[12] can be explained similarly. For Sn impurity atoms in compounds of the type RAl_2, where R denotes a rare-earth ion with a nonzero orbital moment, one must remember that the anisotropic contribution to the magnetic hyperfine interaction depends on the distribution of the magnetic 4*f*-electrons of the ion R^{3+}, whose departure from spherical symmetry is characterized by the quadrupole moment of the 4*f*-electrons. The latter is positive for Sm^{3+} ions but negative for Tb^{3+} and Ho^{3+}; the contributions to the anisotropy of the magnetic hyperfine interaction therefore differ in sign. This accounts for the large differences in the magnitude of the anisotropic component of the field for different compounds of the type RAl_2 (Ref. 1). In $SmAl_2$, for example, the anisotropic contribution due to the nonsphericity of the 4*f*-electrons adds to the contribution from the nonsphericity of the density distribution for the Sn valence electrons, so that the anisotropic component of the hyperfine field is particularly large.

[1] N. N. Delyagin, V. I. Krylov, N. I. Moreva, *et al.*, Zh. Eksp. Teor. Fiz. **88**, 300 (1985) [Sov. Phys. JETP **61**, 176 (1985)].

[2] G. LeCaer, B. Malaman, G. Venturini, *et al.*, J. Phys. **F15**, 1813 (1985).

[3] F. J. Darnell, W. H. Cloud, and H. S. Jarrett, Phys. Rev. **130**, 647 (1963).

[4] M. K. Wilkinson, N. S. Gingrich, and C. G. Shull, J. Phys. Chem. Sol. **2**, 289 (1957).

[5] A. E. Austin, E. Adelson, and W. H. Cloud, Phys. Rev. **131**, 1511 (1963).

[6] H. A. Alperin, P. J. Brown, and R. Nathans, J. Appl. Phys. **34**, 1201 (1963).

[7] S. L. Pinjare and K. V. S. Rama Rao, J. Phys. **F14**, 2185 (1984).

[8] T. A. Bither, P. H. L. Walter, W. H. Cloud, *et al.*, J. Appl. Phys. **33**, 1346 (1962).

[9] C. Blaauw, G. R. Mackay, and W. Leiper, J. Magn. Magn. Mat. **7**, 234 (1978).

[10] N. N. Delyagin, V. I. Krylov, and V. I. Nesterov, Zh. Eksp. Teor. Fiz. **79**, 1049 (1980) [Sov. Phys. JETP **52**, 532 (1980)].

[11] N. N. Delyagin, G. T. Mudzhiri, V. I. Nesterov, and A. K. Churakov, Zh. Eksp. Teor. Fiz. **89**, 2149 (1985) [Sov. Phys. JETP **62**, 1240 (1985)].

[12] S. I. Reĭman, N. I. Rokhlov, I. N. Rozantsev, and F. D. Khamdamov, Izv. Akad. Nauk SSSR Ser. Fiz. **50**, 2392 (1986).

Translated by A. Mason