Hyperfine magnetic fields at the ^{57}and ^{119}Sn nuclei in the antiferromagnet $FeSn_2$ under pressure

I. N. Nikolaev, N. N. Delyagin, V. I. Nesterov, V. P. Potapov, and I. Yu. Bezotosnyĭ

Moscow Engineering Physics Institute
(Submitted 13 July 1977)
Zh. Eksp. Teor. Fiz. **74**, 640–645 (February 1978)

Gamma-resonance spectroscopy is used to investigate the pressure (up to 14 kbar) and temperature dependences of the hyperfine magnetic fields at the nuclei ^{57}Fe and ^{119}Sn in the antiferromagnetic intermetallic compound $FeSn_2$. At 77 K the hyperfine fields at ^{57}Fe and ^{119}Sn are respectively 153.1 ± 0.3 and 35.7 ± 2.5 kOe, and the temperature dependences of the fields are similar. The experimental dependences of the fields are similar. The experimental dependences of the relative changes $\Delta H/H$ of the hyperfine fields on the pressure are the same for ^{57}Fe and ^{119}Sn. The method of temperature scanning the value of the Mössbauer effect is used to determine the pressure-induced shift of the Neel temperature: $\partial T_N/\partial p = 1.7\pm0.4$ deg/kbar. After introducing the correction for the $T_N(p)$ dependence, the value $\Delta H/H\Delta p = (3.2\pm0.4)\times10^{-3}$ kbar^{-1} is obtained for the fields at the nuclei ^{57}Fe and ^{119}Sn. This result means that in the antiferromagnetic $FeSn_2$ matrix there are no competing contributions to the field at the ^{119}Sn nuclei, and the changes of the fields at both ^{57}Sn and ^{119}Sn are proportional to the changes of the magnetizations of the magnetic sublattices.

PACS numbers: 76.80.+y, 75.50.Ee, 62.50.+p

In metallic magnets, the hyperfine magnetic fields at the nuclei of the "magnetic" atoms, which have intrinsic magnetic moments, are the result of polarization of the electrons of their inner shells and of the collectivized electrons of the conduction band. For nonmagnetic atoms, the hyperfine fields are determined by the neighboring magnetic atoms and are sums of contributions of equal magnitude and opposite sign, the relation between these contributions being dependent on the atomic number of the element and on the distribution of the magnetic moments among the coordination spheres. For the ^{119}Sn atoms the contributions were determined empirically,[1] but the interpretation of these regularities is unclear in many respects. For the ^{57}Fe atoms, in turn, even the signs of the contributions to the hyperfine fields from the polarization of the conduction electrons are unknown.

Important information on the mechanisms that form the hyperfine fields can be obtained in experiments in which high pressures are used. The number of such experiments is still small, especially for nonmagnetic atoms. A number of investigations[2-6] have been made, by the Mössbauer spectroscopy method, of the effect of pressure on the magnetic fields at the ^{57}Fe and ^{119}Sn nuclei in certain ferromagnets. It was shown, in particular, that the relative changes of the field under pressure are larger for Sn by approximately an order of magnitude than the relative changes of the corresponding magnetizations. This means that the contributions to the field, which are close in magnitude and opposite in sign, have substantially different radial dependences. For the fields at the ^{57}Fe nuclei it was possible in some cases to determine the signs of the aforementioned contributions from the conduction-electron polarization.[3,5]

In the present paper we have measured the dependences of the hyperfine magnetic fields on the pressure in the antiferromagnetic intermetallic antiferromagnet. Moreover, in this case the measurements can be carried out for both ^{57}Fe and ^{119}Sn, so that the changes in the fields at the nuclei of a magnetic and nonmagnetic atom can be compared in a single system.

The hyperfine interaction in $FeSn_2$ at normal pressure was investigated in [7-9], and the data on the magnetic structure of $FeSn_2$ were published in[10,11].

EXPERIMENT

To produce an ordered $FeSn_2$ alloy of stoichiometric composition, the required amounts of the components, of 99.99% purity, were smelted in vacuum. The ingot was then subjected to a homogenizing annealing at ~1000°C for 30 hours. The ingot was ground into a powder which was annealed in several steps at 450 ±10°C for two weeks. In the course of annealing the powder was periodically stirred. The annealing was stopped when the shapes of the Mössbauer spectra of the selected samples stopped changing.

The Mössbauer resonant-absorption spectra were measured with spectrometers operating at constant velocities and constant acceleration. The γ-ray sources were ^{57}Co in a Cr matrix and ^{119}Sn in $BaSnO_3$. The sources were at room temperature. The technique of producing and measuring the hydrostatic pressures is described in [2].

To interpret the results we needed data on the effect of pressure on the Neel temperature T_N. These data were obtained by the method of temperature scanning of the Mössbauer spectrum of the ^{57}Fe nuclei, with the high-pressure chamber placed in a transformer-oil bath and heated by an external oven. The sample temperature in the chamber was determined accurate to ±0.3°.

Under normal pressure, the absorption spectra were measured at $T = 77$ K and in the temperature range 291–400 K. The determination of the hyperfine structure parameters for ^{119}Sn was made complicated by the

 0038-5646/78/4702-0337$02.40

presence of a quadrupole interaction whose energy at temperatures close to T_N is comparable with the energy of the magnetic hyperfine interaction; as a result, the hyperfine structure of the spectra was not fully resolved. This led to a certain ambiguity in the determination of the hyperfine structure parameters, since the mutual orientation of the magnetic hyperfine field and of the electric field gradient tensor axes is not known. In the analysis of the spectra we estimated the additional error due to this uncertainty and included it in the total error.

No such difficulty arose in the case of ^{57}Fe, since the ^{57}Fe spectra revealed a symmetrical sextet of hyperfine structure components, and the quadrupole shift of the components did not exceed 0.05 mm/sec.

RESULTS AND DISCUSSION

1. Hyperfine magnetic field at ^{57}Fe and ^{119}Sn nuclei at normal pressure

The hyperfine magnetic fields at the ^{57}Fe nuclei are equal to 153.1 ± 0.3 kOe at T = 77 K and 111.4 ± 0.3 kOe at T = 297 K. These values agree with the data of[7-9]. The isomer shift at 297 K is 0.63 ± 0.01 mm/sec.

The absorption spectra for ^{119}Sn are shown in Fig. 1. The hyperfine magnetic fields for ^{119}Sn are 35.7 ± 2.5 kOe at T = 77 K and 26.8 ± 2.6 kOe at T = 291 K. The quadrupole splitting measured in the paramagnetic phase at T = 296.8 K is 0.85 ± 0.02 mm/sec; the isomer shift at T = 297 K is 2.10 ± 0.01 mm/sec.

Figure 2 shows the temperature dependences of the relative magnetic fields $H(T)/H(77)$. Within the limits of the measurement accuracy, these plots are the same for Fe and Sn and can be represented (at $T/T_N > 0.77$) by the power-law function

$$H(T)/H(77) = D(1-T/T_N)^{\beta}, \qquad (1)$$

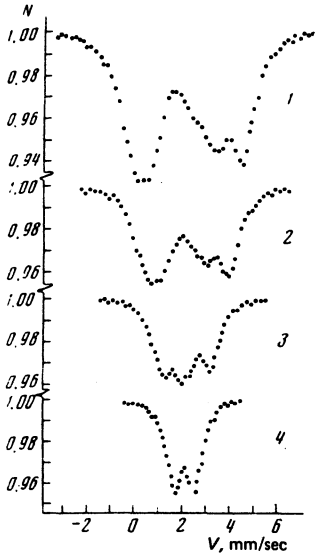

FIG. 1. Mössbauer spectra for the nuclei ^{119}Sn in $FeSn_2$: 1–77 K, 2–291.2 K, 3–365.1 K, 4–396.8 K. The statistical errors do not exceed the dimensions of the points

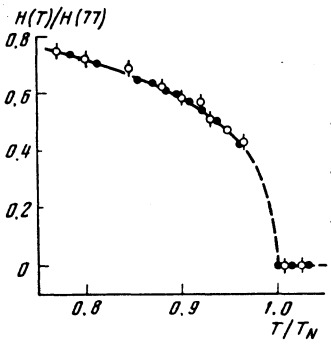

FIG. 2. Temperature dependences of the hyperfine magnetic fields at the ^{57}Fe nuclei (dark circles) and ^{119}Sn (light circles) in relative coordinates.

where D = 1.17 ± 0.01, β = 0.32 ± 0.01, T_N = 378.0 ± 0.3K. In the interpretation of the data on the pressure dependence of the hyperfine fields we use formula (1) to take into account the effect of the pressure on T_N.

At T = 77 K the ratio of the hyperfine field at the ^{57}Fe nuclei to the atomic magnetic moment of Fe [μ = (1.6 ± 0.1)μ_B[10]] is equal to 96 kOe/μ_B (μ_B is the Bohr magneton). Comparison of this quantity with the analogous ratio for other alloys of iron[12] shows that the hyperfine field at the ^{57}Fe nuclei in $FeSn_2$ is practically completely determined by the intrinsic magnetic moment of the Fe atom (the dipole field, according to our estimates, is 4.2 kOe). Therefore the behavior of the hyperfine field at the ^{57}Fe nuclei should reflect the behavior of the intrinsic magnetic moment of the Fe atom.

The existence of a hyperfine field at the ^{119}Sn and $FeSn_2$ nuclei calls for a special analysis. According to the data of[10,11] the $FeSn_2$ compound has a tetragonal structure C16. The magnetic moments of the Fe atoms are parallel to one another and are directed along fourfold axes. The nearest magnetic neighbors of the Sn atom are four Fe atoms, with magnetic moments that are pairwise oppositely directed. Thus, the first coordination sphere of the Sn atom has a zero moment and should therefore not contribute to the hyperfine field. For the same reason, there are neither contributions from the more remote spheres nor a dipole contribution.

If the data on the crystal structure of the $FeSn_2$ are accurate enough and the Sn atoms are indeed located at exactly equal distances from the neighboring Fe atoms with oppositely oriented spins, then to explain the onset of the hyperfine field we must go beyond the framework of simple geometrical considerations. Namely we must call attention to the fact that the distribution of the electrons around the Sn atom is strongly aspherical (this is manifest by the appreciable quadrupole interaction and is the consequence of the asymmetrical arrangement of the atoms is the nearest coordination sphere of Sn). One cannot exclude here the possibility that the chemical bond of the Sn atoms is covalent to a considerable degree. Then the hyperfine field at the ^{119}Sn nuclei can be produced if the overlap of the wave functions of the external s electrons of the Sn with the $3d$ electrons of the Fe causes the appearance of a spin-polarization vector component directed along the chemical bond. In this case the vector sum of the polariza-

tion in the region of the Sn-atom nucleus can become different from zero.

2. Hyperfine magnetic fields at the ^{57}Fe and ^{119}Sn nuclei at high pressures

The Mössbauer spectra for the nuclei ^{57}Fe and ^{119}Sn were measured at a pressure up to 14 kbar at a temperature 297 K, and control measurements were made also at $T = 77$ K. The experimental pressure dependences of the relative changes $\Delta H/H$ of the hyperfine fields are shown in Fig. 3 (line 1). It is seen that, within the limits of errors, the plots are the same for both nuclei. It appears that the agreement of that of the pressure dependence of $\Delta H/H$ for ^{57}Fe and ^{119}Sn means that the changes of H for Sn (as well as for Fe) are directly proportional to the changes of the magnetic moments of the Fe atoms.

This result is in sharp contrast with the previously obtained[2,4,6] data for ^{119}Sn in metallic ferromagnets, where the values of $\Delta H/H\Delta p$ exceeded by approximately one order of magnitude the relative changes of the magnetizations $\Delta\sigma/\sigma\Delta p$. This difference agrees with the interpretation proposed in [4,6], according to which the strong $H(p)$ dependence is due to the difference between the radial dependences of two competing contributions to the hyperfine field. As mentioned above, in the antiferromagnetic $FeSn_2$ all the coordination spheres of the Sn atom have zero moments, and therefore there are no such competing contributions. The field at the ^{119}Sn nucleus therefore follows the variation of the magnetic moment of the Fe atom. This agrees also with the absence of any anomaly in the temperature dependence of the magnetic field for Sn (Fig. 2).

The experimental pressure dependences of $\Delta H/H$ are determined by two different effects: 1) the influence of the pressure on the magnetic moments of the Fe atoms, and 2) the change of the magnetization of the sublattices because of the shift of the Neel temperature. The contribution of the second of these effects depends significantly on the proximity of the measurement temperature to T_N. If the functions $H(T)$ and $T_N(p)$ are known, then the contribution of the second effect can be excluded.

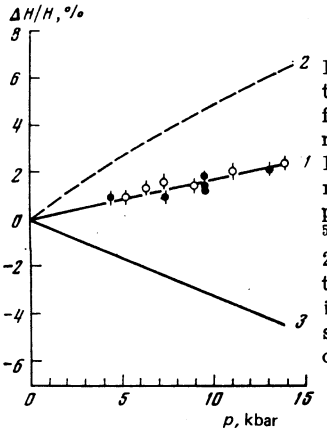

FIG. 3. Plots of the relative changes of the hyperfine magnetic fields at the nuclei ^{57}Fe and ^{119}Sn in $FeSn_2$ on the pressure at room temperature: 1—experiment (dark circles—^{57}Fe, light circles —^{119}Sn), 2—calculation with only the influence of $T_N(p)$ taken into account, 3—result of subtracting the ordinates of lines 1 and 2.

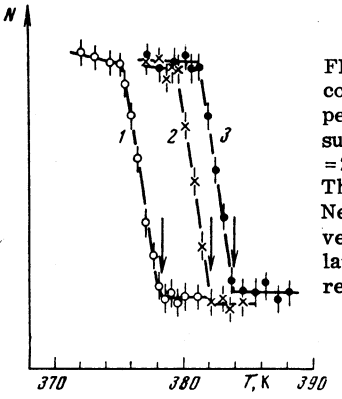

FIG. 4. Plots of the pulse counting rates against temperature at different pressures: 1—$p = 1$ atm, 2—$p = 2$ kbar, 3—$p = 3.2$ kbar. The arrows indicate the Neel temperatures. The velocity of the source relative to the absorber corresponds to resonance.

Figure 4 shows typical plots of the temperature scanning of the Mossbauer effect, as measured at the ^{57}Fe nuclei for different pressures. From the shift of these curves we obtained $\partial T_N/\partial p = 1.7 \pm 0.4$ deg/kbar. Assuming that the coefficients D and β of formula (1) do not depend on the pressure,[3] we have plotted the dashed line 2 in Fig. 3 with only the $T_N(p)$ effect taken into account, and then obtained, by subtracting the ordinates of the lines 1 and 2, the explicit pressure dependence of $\Delta H/H$ of interest to us (line 3). It is seen that when the pressure is increased the hyperfine fields, and hence the magnetic moments of the Fe atoms, decrease.

The correctness of this method of determining the explicit $H(p)$ dependence was verified by control measurements made at $T = 77$ K, which corresponds to $T/T_N = 0.2$. At $T = 77$ K the shift of T_N has no substantial effect on the sublattice magnetization. As expected, the value of H for ^{57}Fe decreases under pressure, in full agreement with the results obtained at room temperature.

From the slope of the line 3 (Fig. 3) we obtained for ^{57}Fe and ^{119}Sn the value $\Delta H/H\Delta p = (-3.2 \pm 0.4) \times 10^{-3}$ kbar^{-1}. As already mentioned, for ^{57}Fe this value should correspond to a change in the intrinsic magnetic moment of Fe. The field at the ^{119}Sn nuclei can in principle change also on account of the change of the electron configuration of the Sn atom, i.e., of the effective number of the external s electrons. We measured for ^{119}Sn the dependence of the isomeric shift on the pressure. Despite the large relative measurement errors, it can be stated that when the pressure is increased the electron density in the region of the Sn nuclei decreases (this behavior of the isomeric shift is typical of Sn in metallic systems[15]). The agreement of the pressure dependences of $\Delta H/H$ for Sn and Fe allows us, however, to conclude that in this case the contribution due to the change of the electron configuration of Sn is negligibly small.

The relatively strong $H(p)$ dependence obtained for ^{57}Fe in the case of $FeSn_2$ seems unexpected. The point is that at pressures up to ~59 kbar a substantial "compression" is experienced mainly by the electrons of the outer atomic shells, while in metallic systems it is the

conduction electrons that are compressed. At the same time, in metallic antiferromagnets the average polarization of the conduction electrons is zero, and the results of [5], where the field at the ^{57}Fe nuclei in the antiferromagnetic alloy Pt_3Fe was practically independent of the pressure, were explained naturally from this point of view. It appears that $FeSn_2$ is not a "good" metal and the strong dependence of the hyperfine field at the ^{57}Fe nuclei is connected with partial localization of the external magnetic electrons of the Fe atoms in directed chemical bonds.

In conclusion, the authors thank V. P. Mar'in for help with a number of experiments.

[1]N. N. Delyagin and É. N. Kornienko, Zh. Eksp. Teor. Fiz. **61**, 1946 (1971) [Sov. Phys. JETP **34**, 1036 (1972)].
[2]I. N. Nikolaev, V. P. Potapov, and V. P. Mar'in, Zh. Eksp. Teor. Fiz. **67**, 1190 (1974) [Sov. Phys. JETP **40**, 591 (1975)].
[3]I. N. Nikolaev, L. S. Pavlyukov, and V. P. Mar'in, Zh. Eksp. Teor. Fiz. **69**, 1844 (1975) [Sov. Phys. JETP **42**, 936 (1975)].
[4]I. N. Nikolaev, V. P. Potapov, and N. N. Delyagin, Zh. Eksp. Teor. Fiz. **70**, 241 (1976) [Sov. Phys. JETP **43**, 125 (1976)].
[5]I. N. Nikolaev, L. S. Pavlyukov, V. P. Potapov, and V. P. Mar'in, Fiz. Tverd. Tela (Leningrad) **18**, 1198 (1976) [Sov. Phys. Solid State **18**, 692 (1976)].
[6]I. N. Nikolaev and V. P. Potapov, Zh. Eksp. Teor. Fiz. **72**, 1600 (1977) [Sov. Phys. JETP **45**, 840 (1977)].
[7]V. I. Nikolaev, Yu. I. Shcherbina, and S. S. Yakimov, Zh. Eksp. Teor. Fiz. **45**, 1277 (1963) [Sov. Phys. JETP **18**, 878 (1964)];V. I. Nikolaev, Yu. I. Scherbina, and A. I. Karchevskiĭ, Zh. Eksp. Teor. Fiz. **44**, 775 (1963) [Sov. Phys. JETP **17**, 524 (1963)].
[8]G. Fabri, E. Germagnoli, M. Musei, and G. C. Locati, Nuovo Cimento B **40**, 178 (1965).
[9]G. Trumpy, E. Both, C. Djega-Mariadassou, and P. Lecocq, Phys. Rev. B **2**, 3477 (1970).
[10]W. Nicholson and E. Friedman, Bull. Am. Phys. Soc. **8**, 43 (1963).
[11]P. K. Iyengar, B. A. Dasannacharya, P. R. Vijayaraghavan, and A. P. Roy, J. Phys. Soc. Jpn. **17**, 247 (1962).
[12]M. B. Stearns, Phys. Rev. B **4**, 4081 (1971); V. Niculescu, K. Raj, J. I. Budnick, T. J. Burch, W. A. Hines, and A. H. Menotti, Phys. Rev. B **14**, 4160 (1976).
[13]V. N. Panyushkin, Fiz. Tverd. Tela (Leningrad) **10**, 1915 (1968) [Sov. Phys. Solid State **10**, 1515 (1968)].

Translated by J. G. Adashko

Rearrangement of the energy spectrum of $Pb_{1-x}Sn_xSe$ as a result of band inversion under pressure

N. B. Brandt, O. N. Belousova, V. P. Zlomanov, Ya. G. Ponomarev, E. P. Skipetrov, and V. I. Shtanov

Moscow State University
(Submitted 16 August 1977)
Zh. Eksp. Teor. Fiz. **74**, 646–657 (February 1978)

An investigation was made of the oscillatory and galvanomagnetic effects in single-crystal samples of *n*-type $Pb_{1-x}Sn_xSe$ ($x = 0.125$) at pressures up to 16 kbar. The dependences of the cyclotron masses at the Fermi level on the band gap ϵ_g were asymmetric relative to $\epsilon_g = 0$, as predicted in the theories of Dimmock and Martinez. The electron Fermi surface became spherical for negative values of ϵ_g. The experimental results obtained were combined with the data of other authors in a calculation of the parameters of the Dimmock dispersion law of carriers at the point L in the Brillouin zone.

PACS numbers: 71.25.Pi, 72.15.Gd, 62.50.+p

INTRODUCTION

Lead selenide (PbSe) and its alloys $Pb_{1-x}Sn_xSe$ ($x < 0.43$) crystallize in the NaCl lattice and are semiconductors with a narrow direct gap ϵ_g at the point L in the Brillouin zone. In the case of PbSe and $Pb_{1-x}Sn_xSe$ with $x < x_0$ ($x_0 = 0.15$ at $T = 4.2$°K) the terms L_6^- and L_6^+, which correspond to the bottom of the conduction band and the top of the valence band at atmospheric pressure,[1] become inverted at higher pressures.[2-5] The transition to the zero-gap state [$\epsilon_g \equiv E(L_6^-) - E(L_6^+) = 0$] at a pressure $p = p_0$, which depends on the composition x and temperature T, is accompanied by vanishing of the effective carrier masses $m^*(0)$ at the bottom of the conduction band and at the top of the valence band. The effective masses at the Fermi level $m^*(\epsilon_F)$ are affected much less by transition to the zero-gap state and the relative reduction in these masses decreases with increasing carrier density in the bands.[5]

The nature of the rearrangement of the carrier spectrum as a result of inversion of the terms at L depends on the strength of the interaction of the inverted terms with the more distant bands at the point L.[1-4,6] If this interaction can be ignored, the carrier dispersion law is of the Kane type[7] and the sign of the band gap ϵ_g is unimportant. Then, all the ϵ_g-dependent quantities vary symmetrically relative to the value $\epsilon_g = 0$ [the effective masses $m^*(\epsilon_F)$ pass through a minimum and the Fermi energy ϵ_F passes through a maximum if the carrier

 0038-5646/78/4702-0340$02.40