Magnetic hyperfine interaction of ^{119}Sn impurity atoms in hexagonal Fe_3Ge

N. N. Delyagin, Yu. D. Zonnenberg, and V. I. Nesterov

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

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The Mössbauer γ spectroscopy method was used to investigate the magnetic hyperfine interaction of the ^{119}Sn impurity atoms in the hexagonal modification of the ferromagnetic alloy Fe_3Ge. At 77°K the magnetic hyperfine field at the Sn atoms occupying the Ge sites was -174.0 ± 1.5 kOe; this value was considerably greater than the hyperfine field at the Sn atoms in the ferromagnetic alloy Fe_3Sn with the same structure. Increase in temperature caused the hyperfine magnetic field at Sn in Fe_3Ge to decrease much more rapidly than the hyperfine field at ^{57}Fe or the magnetization. The results were explained by a strong radial dependence of the negative contribution to the hyperfine field at the Sn atoms in metallic ferromagnets. An analysis was made of some other experimental data indicating a strong radial dependence of that component of the hyperfine field which was due to the nearest magnetic neighbors of the Sn atoms. A change in the orientation of the magnetic moments in Fe_3Ge at 380°K did not affect significantly the hyperfine field at Sn; at this temperature the anisotropic contribution to the hyperfine field did not exceed 1 kOe.

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1. INTRODUCTION

In the case of an atom which (like Sn) does not have an intrinsic magnetic moment the magnetic hyperfine interaction in a ferromagnetic crystal is entirely due to the magnetic environment. Explanation of the mechanisms of the transfer of the spin density from the magnetic to nonmagnetic atoms is one of the central problems in the theory of magnetic hyperfine fields. The current status of the theory has recently been reviewed by Price *et al.*[1] It is usually assumed that the transfer of the spin density in metallic ferromagnets involves polarized electrons from the conduction band. Attempts to calculate theoretically the hyperfine fields at nonmagnetic atoms are based on an analysis of "oscillations" of the spin or charge density of conduction electrons polarized by the exchange interaction with localized magnetic moments.

Unfortunately, there are as yet no calculation methods for determining the hyperfine fields with a precision sufficient for quantitative interpretation of the experimental data. In particular, considerable difficulties appear in connection with the need to allow for the characteristics of the interaction between the conduction electrons and the nonmagnetic atom potential. The importance of this potential follows even from systematics of the hyperfine fields at impurity atoms in homogeneous ferromagnetic matrices[2]; the dependence of the hyperfine field on the electron structure of a nonmagnetic atom appears also clearly in a systematic analysis of the data on ordered ferromagnetic alloys.[1] We may assume that allowance for the actual properties of the atomic potential is particularly important in discussing the interactions of a nonmagnetic atom with its nearest magnetic neighbors.

Some data on the mechanisms of formation of the hyperfine field at nonmagnetic atoms have been obtained by an empirical analysis of the experimental results. Such an analysis is based on the representation of the hyperfine field H by the sum over the coordination spheres:

$$H(\text{kOe})=\sum n_i\mu_i h_i, \tag{1}$$

where n_i is the number of atoms in the i-th sphere; μ_i is their average atomic moment (μ_B); h_i is the partial contribution to H made by the i-th sphere per one atom (kOe/μ_B). In general, the summation in Eq. (1) is over all the spheres but naturally at large distances the partial contributions h_i are negligible. In practice, use is made of simplified variants of Eq. (1) with a small number of parameters. For example, the following empirical formula is obtained in Ref. 3 for tin in metallic ferromagnets and antiferromagnets with the bcc structure:

$$H(\text{kOe})=-218\mu_1+9\mu_2+165\bar{\mu}, \tag{2}$$

where μ_1 and μ_2 are the average atomic moments in the first and second spheres; $\bar{\mu}$ is the average atomic magnetic moment of the alloy. It follows from Eq. (2) that the nearest neighbors of a tin atom are responsible for the large negative contribution to the hyperfine field; the magnetic atoms in the more distant sphere give an overall positive contribution comparable—in the absolute sense—with the negative contribution. (A similar result was obtained by a somewhat different method in a recent paper of Campbell *et al.*[4]) This representation of the hyperfine field explains many features of the magnetic hyperfine interaction of tin in metallic ferromagnets and antiferromagnets.[3,4] It is necessary to stress that the empirical formulas analogous to Eq. (2) apply only to systems with the same structure and similar interatomic distances. The partial contributions h_i (and, consequently, the coefficients in the empirical formula) undoubtedly depend on the distance between the atoms. This dependence is of paramount im-

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portance in the interpretation of the data on the magnetic hyperfine interaction in metallic systems.

Important data on the radial dependence of the partial contributions to H of tin were obtained recently by Nikolaev *et al.*[5,6] The unusually strong pressure dependence of H obtained by them shows that the negative and positive contributions to H vary differently with the interatomic distance. An analysis of the results in Ref. 6 shows that a reduction in the distance between the atoms enhances greatly the negative contribution to the hyperfine field.

The strong radial dependence of the negative contribution should appear also in other effects associated with the magnetic hyperfine interaction in metallic systems. For example, allowance for this dependence makes it possible to explain in a natural manner the anomalous temperature dependences of H for the tim impurity atoms in iron and cobalt matrices.[7] In this case the distance between the atoms varies as a result of the thermal expansion of the lattice. A consistent analysis of the temperature dependences of the hyperfine fields can give useful information on the radial dependence of the partial contributions. These dependences can also be investigated by comparing the hyperfine fields in systems with the same structure but with different distances between the atoms. With this in mind we investigated the magnetic hyperfine interaction of tin impurity atoms in the Fe_3Ge matrix and compared the results obtained with the data for the isostructural Fe_3Sn matrix.

2. PROPERTIES OF HEXAGONAL Fe_3Ge, EXPERIMENTAL METHOD, AND THE MAIN RESULTS

The ordered ferromagnetic alloy Fe_3Ge has two modifications: the cubic $L1_2$ and hexagonal DO_{19}. The hexagonal modification is stable above 970° K but the transition to the cubic phase is very slow, so that the hexagonal form can be investigated in a wide range of temperatures. The magnetic properties of the hexagonal Fe_3Ge have been studied in detail.[8,9] The Curie temperature deduced from the magnetic measurements is 636° K and that deduced from the temperature dependence of the magnetic hyperfine interaction of ^{57}Fe is 646° K (Ref. 9); the magnetic moment of the iron atom is 2.03 μ_B (Ref. 9). Above 380° K the magnetic moments are parallel to the c axis of the crystal; at lower temperature the spins are rotated to the basal plane. The transition is accompanied by a strong reduction in the external field, needed to saturate the magnetization. According to the results of Drijver *et al.*,[9] the saturation field near 380° K does not exceed 1 kOe whereas far from the transition temperature it reaches 6 kOe. The fullest data on the magnetic hyperfine interaction of ^{57}Fe in the hexagonal form of Fe_3Ge are given in the paper of Drijver *et al.*[9]

We investigated the magnetic hyperfine interaction of the ^{119}Sn impurity atoms in the hexagonal Fe_3Ge by the Mössbauer γ spectroscopy method. Samples were prepared by fusing the components (of at least 99.98% purity) in high vacuum; tin enriched with the ^{119}Sn isotope to 91.3% was introduced into the iron. Ingots were remelted several times and then annealed at 950° C for 30 *h*. Powders were prepared from the ingots, annealed at 830° C for 8 h, and quenched in water. The quality of the samples was checked by recording the Mössbauer absorption spectra of ^{57}Fe; the results of these measurements agreed well with those of Drijver *et al.*[9] Several samples with 0.3–0.7 at.% Sn were prepared. The parameters of the absorption spectra at 77 and 292° K were identical for all the samples and, therefore, the temperature dependence of the hyperfine field was measured only for one sample containing 0.7 at.% Sn.

An attempt was also made to prepare a solid solution of tin in the cubic modification of Fe_3Ge but it was unsuccessful. After prolonged annealing at 600° C (which was necessary to obtain the cubic structure in the alloy) the phases formed were of unknown composition. An analysis of the absorption spectra of ^{119}Sn indicated that tin did not form a solid solution is the cubic modification of Fe_3Ge. (For the Fe_3Sn alloy of similar composition only the hexagonal ordered structure is known.) We shall consider below only the results for the hexagonal Fe_3Ge.

The spectra of the resonance absorption of the 23.9 keB γ rays by ^{119}Sn were determined using a $CaSnO_3$ or $BaSnO_3$ source. The temperature of a sample (in an oven or in a cryostat) was kept constant to within at least ±0.02° K by an electronic control system. The hyperfine structure parameters were determined by the usual procedure of approximation of the spectra with a sum of Lorentzian lines.

Figure 1 shows the absorption spectrum of ^{119}Sn measured at 77° K. The spectrum has a completely resolved hyperfine structure; the widths and the intensities of the components agree with the theory for a single value of the hyperfine field and random orientation of the magnetization in the absorber. The quadrupole shift of the hyperfine structure components did not exceed 0.05 mm/sec. Measurements in an external magnetic field of 10 kOe intensity showed that the sign of the field was negative. The magnetic hyperfine field of tin in the hexagonal form Fe_3Ge was found to be $-174.0 + 1.5$ kOe at 77° K. The temperature dependence of the hyperfine field is shown in Fig. 2. For comparison, this figure includes also the temperature dependence of the hyperfine field at ^{57}Fe, which is practically identical with the temperature dependence of the magnetization.[9] We can see that the hyperfine field of tin decreases more rapidly on increasing temperature than does the hyperfine

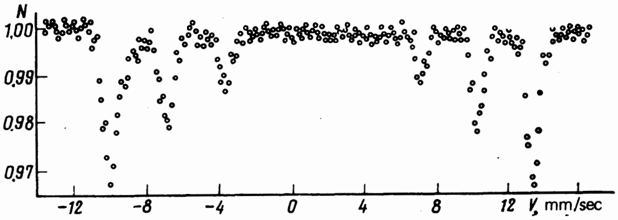

FIG. 1. Mössbauer resonance absorption spectrum of ^{119}Sn in Fe_3Ge at 77°K.

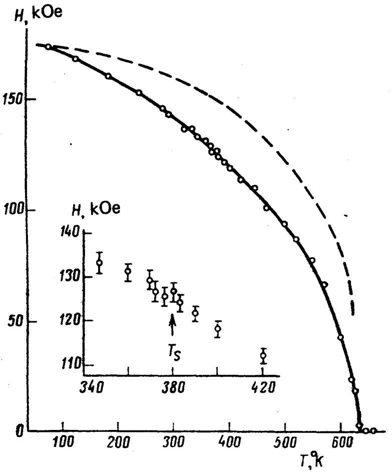

FIG. 2. Temperature dependence of the magnetic hyperfine field of ^{119}Sn in Fe_3Ge. The dashed curve is the temperature dependence of the hyperfine field at ^{57}Fe (Ref. 9) normalized to the hyperfine field for ^{119}Sn at 77°K. Bottom left corner shows, on an enlarged scale, the dependence $H(T)$ for ^{119}Sn near the temperature $T_S = 380$°K corresponding to the transition involving a change in the spin orientation.

field at ^{57}Fe. The Curie temperature deduced from the temperature dependence of the hyperfine field at tin is 636.5 ± 1.5° K, which agrees with the value 636 ± 1° K obtained by Drijver *et al.*[9] from the magnetization measurements. This agreement confirms that tin impurities form a solid solution in the hexagonal Fe_3Ge matrix.

The atoms of tin and germanium have the same configuration of the outer electrons and, therefore, we may expect the tin atoms in the Fe_3Ge lattice to become localized at the germanium sites. Such localization is particularly likely because of the existence in the Fe–Sn system of the ordered Fe_3Sn phase with the same structure as that of the hexagonal Fe_3Ge. The hypothesis of the localization of the tin atoms at the germanium sites is in agreement with the general systematics of hyperfine fields[3]: a large negative field at the nucleus of a tin atom corresponds to a large negative moment of the first coordination sphere at a germanium site.

3. DISCUSSION OF RESULTS

1. Comparison of hyperfine fields in Fe_3Ge:Sn and Fe_3Sn

The ferromagnetically ordered alloys Fe_3Ge and Fe_3Sn have the same hexagonal structure and similar magnetic properties. The magnetic moment of an iron atom in Fe_3Sn is 2.27 μ_B, which is only 10% greater than in the hexagonal Fe_3Ge. The magnetic hyperfine fields at the iron atoms measured at low temperatures are almost the same: −260.9 kOe in Fe_3Ge (Ref. 9) and −268 kOe in Fe_3Sn (Ref. 10).

If we assume a proportionality between the hyperfine field at a nonmagnetic atom and the magnetization of the matrix, we can expect similar values of H for tin in Fe_3Ge and Fe_3Sn. However, the hyperfine fields are in fact quite different: the field for tin in Fe_3Sn at 77° K is −103 kOe (Ref. 10), which is considerably less than −174 kOe found by us for tin in Fe_3Ge. The negative hyperfine field at tin in Fe_3Ge is approximately 70 kOe greater than in Fe_3Sn in spite of the fact that the atomic magnetic moment is 10% greater in Fe_3Sn. In a more precise comparison of the hyperfine fields in the two matrices we can allow for this difference between the atomic moments assuming that (other conditions being equal) the observed hyperfine field is proportional to the magnetization. After introduction of an appropriate correction the difference between the hyperfine fields at tin impurities in the two isostructural matrices increases to about 80 kOe.

We shall assume that this difference is due to the strong dependence of the negative contribution to the hyperfine field on the distance between atoms. The ordered Fe_3Ge and Fe_3Sn alloys are similar in respect of the their structure and magnetic properties but have somewhat different lattice constants: $a = 5.17$ Å, $c = 4.22$ Å for Fe_3Ge (Ref. 9) and $a = 5.46$ Å, $c = 4.36$ Å for Fe_3Sn (Ref. 10). The distance between a tin atom and the 12 nearest iron atoms is 2.6 Å in Fe_3Ge and 2.7 Å in Fe_3Sn. Reduction in the distance by about 4% increases the negative contribution to the hyperfine field by about 80 kOe. Such a strong dependence of the partial contribution h_1 on the distance may be unexpected, but (as shown below) it is in agreement with other experimental data, some of which are considered briefly in the introductory paragraphs of the present paper.

The hyperfine fields at tin atoms in metallic ferromagnets may be regarded as the sum of two large contributions of opposite signs. Each of these contributions is usually much greater than the net field H and, therefore, even a relatively small change in one of these contributions may alter greatly the value of H. It has been shown earlier[3] that for interatomic distances close to 2.5–2.6 Å the partial contribution h_1 is approximately −27 kOe/μ_B. In the hexagonal Fe_3Ge a tin atom has 12 nearest Fe neighbors with a magnetic moment of about 2 μ_B. Thus, the negative contribution to H made by the first coordination sphere $n_1\mu_1h_1$ is approximately −650 kOe. This estimate shows directly that the 80 kOe difference between the values of H for tin in Fe_3Ge and Fe_3Sn can be explained if a reduction in the distance r by 4% increases the negative contribution to H by about 12%. Such a relationship between $\Delta h_1/h_1$ and $\Delta r/r$ corresponds to, for example, the r^{-3} dependence of the negative contribution of the distance. It is significant that the same estimate of the radial dependence of the negative contribution follows also from an analysis of the pressure dependence of H in Ref. 6. These estimates are obtained on the assumption that the radial dependence of the positive contribution is negligible. However, if the positive contribution increases on reduction in r, the radial dependence of the negative contribution may be even stronger.

2. Temperature dependence of the hyperfine field

It follows from the results in Fig. 2 that the temperature dependence $H(T)$ for tin in Fe_3Ge is much stronger than the temperature dependences of the magnetization and of the hyperfine fields at ^{57}Fe. Such anomalies of $H(T)$ are typical of tin in metallic ferromagnets. We have recently drawn attention to the fact that in some cases these anomalies may be associated with the thermal expansion of the crystal lattice.[7] Unfortunately, no data are available on the thermal expansion of Fe_3Ge and, therefore, a quantitative analysis of the influence of thermal expansion on the dependence $H(T)$ is in this case impossible. In a rough estimate we shall assume that in the temperature range 77–500° K the relative change in the distance between atoms is close to 10^{-2}. If (as found above) the negative contribution to H is proportional to r^{-3}, such an increase in the distance should reduce H by about 20 kOe. This is only 1.5 times less than the value required to explain fully the observed temperature anomaly of the hyperfine field at tin in Fe_3Ge. We cannot exclude the possibility that Fe_3Ge has a larger thermal expansion coefficient: this may account for the strong temperature dependence of the electric quadrupole interaction of ^{57}Fe found by Drijver *et al.*[9]

We investigated most thoroughly the dependence $H(T)$ close to the temperature $T_S = 380°$ K at which there is a change in the orientation of the magnetic moments in Fe_3Ge. We can see from Fig. 2 that there is no anomaly in the dependence $H(T)$ due to this transition. Hence, the magnetic hyperfine interaction at tin in Fe_3Ge is isotropic and independent of the orientation of the Fe moments relative to the axes of the crystal. The upper limit for the anisotropic contribution to H at tin is 1 kOe, i.e., it represents 0.8% of the total hyperfine field at 380° K.

Near T_S the external magnetic field has a strong influence on the form of the absorption spectrum. In very weak longitudinal fields (of about 50 Oe intensity) there is a strong reduction in the relative intensities of the second and fifth components of the magnetic hyperfine structure, which corresponds to the polarization of a sample along the direction of the γ-ray flux. This confirms the results of Drijver *et al.*[9] on strong reduction in the magnetic anisotropy of the hexagonal Fe_3Ge near the temperature of the change in the spin orientation.

3. Some conclusions

It follows from the experimental data that the negative contribution to the hyperfine field which is governed by the nearest neighbors of a nonmagnetic atom depends on the distance. The radial dependence of the positive contribution is much weaker. The experimental data are obtained only for tin but this conclusion should apply to a greater or smaller degree also to any nonmagnetic atom in a metallic ferromagnet. Estimates of the radial dependence of the negative contribution obtained from an analysis of various experiments give results which are in good agreement. However, we must bear in mind that the experimental data on which these estimates are based are still very limited. We cannot exclude the possibility that the radial dependence of the negative contribution is largely governed by the equilibrium distance between the lattice atoms and by the type of interacting atoms. Obviously, the experiments in which the radial dependence of the partial contributions to the hyperfine field is manifested would be particularly desirable.

The strong radial dependence of the partial contribution h_1 allows us to explain some "anomalous" data on the magnetic hyperfine interaction of tin in metallic ferromagnets. One of these "anomalies" has been reported for tin in the ordered ferromagnetic alloy Co_2TiSn with the bcc structure (see, for example, Ref. 11). The hyperfine field at tin in this alloy is positive, which is not in agreement with Eq. (2) predicting a negative value of H. We have drawn attention above to the fact that the impirical formulas such as Eq. (2) are applicable only to systems with similar lattice constants. The lattice constant of the Co_2TiSn alloy is considerably greater than for the majority of the systems considered in the determination of the coefficients in Eq. (2) (Ref. 3). In this alloy the magnetic Co atoms are the nearest neighbors of tin. An increase in the distance between the atoms should be accompanied by a reduction in the negative contribution to H, which is the reason for the anomalous value of H for tin in Co_2TiSn. A similarly large lattice constant is found in the alloy Cu_2MnSn, but the experimental value of H for tin in this alloy is in good agreement with Eq. (2). The nearest neighbors of a tin atom are now the nonmagnetic Cu atoms and, therefore, an increase in the distance does not affect significantly the hyperfine field.

[1] D. C. Price, J. D. Rush, C. E. Johnson, M. F. Thomas, and P. J. Webster, J. Phys. (Paris) **37**, Colloq. 6, C6-317 (1976).

[2] A. E. Balabanov and N. N. Delyagin, Zh. Eksp. Teor. Fiz. **54**, 1402 (1968) [Sov. Phys. JETP **27**, 752 (1968)]; G. N. Rao and A. K. Singhvi, Phys. Status Solidi B **84**, 9 (1977).

[3] N. N. Delyagin and É. N. Kornienko, Zh. Eksp. Teor. Fiz. **61**, 1946 (1971) [Sov. Phys. JETP **34**, 1036 (1972)].

[4] C. C. M. Campbell, T. Birchall, and J. C. Suits, J. Phys. F **7**, 727 (1977).

[5] I. N. Nikolaev, V. P. Potapov, and V. P. Mar'in, Zh. Eksp. Teor. Fiz. **67**, 1190 (1974) [Sov. Phys. JETP **40**, 591 (1975)].

[6] I. N. Nikolaev, V. P. Potapov, and N. N. Del'yagin, Zh. Eksp. Teor. Fiz. **70**, 241 (1976) [Sov. Phys. JETP **43**, 125 (1976)].

[7] N. N. Delyagin, Yu. D. Zonnenberg, É. N. Kornienko, V. I. Krylov, and V. I. Nesterov, Zh. Eksp. Teor. Fiz. **75**, 334 (1978) [Sov. Phys. JETP **48**, 165 (1978)].

[8] K. Kanematsu and T. Ohoyama, J. Phys. Soc. Jpn. **20**, 236 (1965).

[9] J. W. Drijver, S. G. Sinnema, and F. van der Woude, J. Phys. F **6**, 2165 (1976).

[10] G. Trumpy, E. Both, C. Djega-Mariadassou, and P. Lecocq, Phys. Rev. B **2**, 3477 (1970).

[11] N. N. Delyagin, Yu. D. Zonnenberg, and V. I. Nesterov, Fiz. Tverd. Tela (Leningrad) **17**, 3036 (1975) [Sov. Phys. Solid State **17**, 2013 (1975)]; C. C. M. Campbell, J. Phys. F **5**, 1931 (1975).

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