Influence of pressure on effective magnetic fields at tin impurity nuclei in iron and nickel

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The Mössbauer effect was used in an investigation of the influence of pressure (up to 12.5 kbar) on magnetic hyperfine fields acting on Sn^{119} impurity nuclei in Fe and Ni matrices. Pressure increased the field in the Fe matrix and reduced it in Ni. The relative changes in the fields $\Delta H / H \Delta P$ were $(-6.5 \pm 0.7) \times 10^{-3}$ kbar^{-1} in Ni and $(+3.0 \pm 0.7) \times 10^{-3}$ kbar^{-1} in Fe. Pressure reduced the electron density in the region of an Sn impurity nucleus. The results were explained qualitatively on the basis of the model of "competing contributions" making allowance for the difference between the radial dependences of the positive and negative contributions to the hyperfine field.

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INTRODUCTION

Nonmagnetic impurities in ferromagnets and anti-ferromagnets can act as "probes, " which can be used to study the spin polarization of the surrounding electrons. In metal systems it is usually assumed that the magnetic field H acting on nonmagnetic nuclei appears because of the transfer of the spin density to a unit cell of an impurity by conduction electrons. The experimental data on the subject have been analyzed systematically, empirical relationships have been established, and models to explain these relationships have been suggested (see, for example, [1-4]). Nevertheless, a consistent theory of the magnetic hyperfine interaction in metals does not yet exist and, moreover, it is not clear which mechanisms (out of those possible in principle) are important in the generation of hyperfine fields.

One of the unresolved problems is the radial dependence of the contributions to the hyperfine field. The sources of the spin polarization of a nonmagnetic atom are necessarily its neighbors with nonzero magnetic moments. Unfortunately, it has not yet been possible to determine the dependence of the spin polarization on distance although it is clear that without allowance for this dependence a consistent analysis of the experimental results is impossible. The radial dependence of the polarization of conduction electrons is usually considered employing the Ruderman–Kittel–Kasuya–Yosida (RKKY) theory [5] or the theory of Friedel oscillations of the charge density. [6] However, a comparison of these theories with the experimental data (see, for example, [7]) shows that this approach to the interpretation of the results is not sufficiently consistent. It is not yet clear whether this is due to the basic inapplicability of these theories or due to difficulties of formal nature because both the RKKY theory and the theory of charge oscillations are necessarily used in a form which simplifies excessively the real situation. An analysis of the experimental data on the hyperfine fields at Sn atoms in bcc ferromagnets and antiferromagnets [8] has led to the conclusion that the hyperfine field is the algebraic sum of two comparable and large contributions one which is positive and the other negative. It is suggested there that the negative ("local")

contribution should have a much stronger radial dependence than the positive ("collective") contribution.

Clearly, the most direct method for determining the radial dependences of the contributions to the hyperfine fields is provided by an investigation of the dependence of these fields on the pressure $H(P)$. In our earlier work [9] this dependence was investigated by the Mössbauer effect for Sn^{119} in Co_2MnSn. The absence of information on the influence of pressure on the magnetization of these alloys prevented us from giving an unambiguous interpretation of the experimental results. In the present paper we shall report a similar investigation of Sn^{119} impurities in Fe and Ni matrices. These matrices are characterized by well-known values of $\sigma^{-1} \partial \sigma / \partial P$ (σ is the magnetization).

EXPERIMENTAL METHOD

The pressure dependences of the magnetic hyperfine fields at Sn^{119} nuclei in Fe and Ni matrices were determined by the Mössbauer effect at room temperature. Samples were prepared by vacuum melting of 99.9% pure Fe and Ni with metallic tin which was enriched with the Sn^{119} isotope to 85%. The concentration of Sn in both matrices was 0.5 at.%. The alloys were homogenized by annealing at 1000 °C in vacuum for 30 h. Powdered alloys were used to prepare absorbers 300 mg/cm^2 thick. The resonance absorption spectra of 23.8 keV γ rays were measured with a constant-velocity Mössbauer spectrometer using a $Sn^{119}O_2$ source of 5 μCi activity.

A hydrostatic pressure was applied to absorbers in a steel cylinder–piston chamber with beryllium windows for the transmission of γ radiation. The construction of this chamber was described in detail in [10]. The pressure in the chamber was measured with calibrated manganin resistance transducers to within ± 0.1 kbar.

An analysis of the theoretical absorption spectra calculated on a computer indicated that for the hyperfine fields observed at room temperature at Sn^{119} in Fe and Ni the total width of the absorption spectrum and the hyperfine splitting should be linearly related. This enabled us to find the change in the hyperfine fields H

TABLE 1. Experimental data on hyperfine interactions of Sn^{119} in CO_2MnSn, Fe, and Ni matrices and some properties of matrices.

Matrix	H, kG	ε, mm/sec	$(\Delta \sigma/\sigma \Delta P) \times 10^4$, kbar^{-1}	$(\Delta \varepsilon/\Delta P) \times 10^3$, mm·sec^{-1}·kbar^{-1}	$(\Delta H/H \Delta P) \times 10^3$, kbar^{-1}	$K \times 10^4$, kbar^{-1}
Co_2MnSn	97.6	1.403 ± 0.006	...	-1.43 ± 0.43	-2 ± 0.3	...
Ni	18.6	1.47 ± 0.006	$-2.4^{[13]}$	-1.84 ± 0.43	-6.5 ± 0.7	4.9
Fe	-81.0	1.42 ± 0.006	$-2.9^{[13]}$	-1.0 ± 0.8	3 ± 0.7	5.9

Note: Here, H is the hyperfine field, ε is the isomeric shift measured relative to a $Sn^{119}O_2$ source, σ and K are the magnetization and compressibility of the matrix, and $\Delta H = H(P) - H(0)$. The values listed in Table 1 apply at room temperature.

under pressure directly from changes in the total width of the absorption spectrum. In addition to the dependences $H(P)$, we also determined the influence of pressure on the isomeric shift ε, which was proportional to the electron density in the region of an impurity nucleus; the value of ε was found from the center of gravity of the spectrum.

The experimental errors, indicated in the figures and in Table 1, were the statistical errors corresponding to possible variations of the line width and center of gravity in comparisons of the measured and calculated spectra. The time required to determine one spectrum at a fixed pressure was 12–16 h. Before and after the determination of each spectrum we calibrated the velocity using a Co^{57}-in-Cr source and a sodium nitroprusside absorber.

RESULTS AND DISCUSSION

Figure 1 shows typical absorption spectra of Sn^{119} in Ni under normal conditions and at a pressure of 12.5 kbar. The spectra were in the form of doublets and each component consisted of three unresolved lines. Under pressure the spectra became narrower, which indicated a reduction in H. Figure 2 shows the relative changes in H as a function of the pressure $[\Delta H = H(P) - H(0)]$. At $P = 10$ kbar it was found that $- \Delta H/H = 6.5 \pm 0.7\%$; this relative change in H was the largest of those known at present. Figure 3 shows the pressure dependence of the change in the isomeric shift ε; we found that the isomeric shift and, consequently, the electron density in the region of Sn^{119} nuclei, decreased with rising pressure.

Since the pressures were relatively low, it was reasonable to assume that the reduction in ε was in practice

due to a reduction in the density of the "outer" s electrons (conduction electrons).

Figure 4 shows the absorption spectrum of Sn^{119} in Fe under normal conditions. At pressures $P > 1$ atm we measured only the "linear" parts of the outer edges of the spectrum and this was sufficient, as pointed out above, for the determination of ΔH. These edges are shown as straight lines in Fig. 4: they were plotted on the basis of the experimental points by the least-squared method. Clearly, the width of the spectrum increased with pressure, i.e., the hyperfine field H increased. The pressure dependence of $\Delta H/H$, plotted in Fig. 5, indicated that at $P = 10$ kbar the change was $\Delta H/H = 3.0 \pm 0.7\%$. The dependence $H(P)$ obtained for Sn^{119} in Fe agreed, within the limits of the experimental error, with the results reported in[11]. The pressure dependence of the isomeric shift could not be measured accurately for the iron matrix but we could conclude that the shift (as in the case of Ni) decreased with rising pressure. This result was in conflict with the conclusion reached in[11] but in agreement with the results in[12], where it was shown that the isomeric shift of Sn^{119} in Fe under normal pressure decreased when temperature was lowered, i.e., when the crystal lattice was compressed thermally.

The main results of the measurements and some of the characteristics of the investigated matrices are listed in Table 1. An analysis of the results obtained led to the following conclusions:

1) The values of $\Delta H/H \Delta P$ are approximately an order of magnitude higher than the values of the relative changes in the magnetization $\Delta \sigma/\sigma \Delta P$. Consequently, the changes in the magnetization are not the main cause of the changes in H.

2) The value of $\Delta H = H(P) - H(0)$ is always negative irrespective of the sign of H, i.e., the positive hyper-
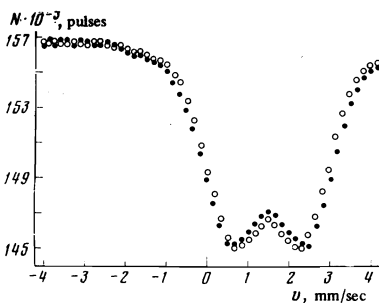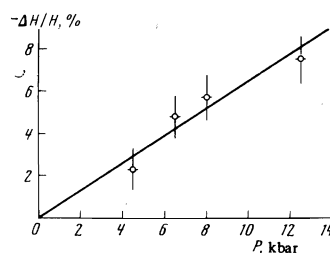

FIG. 1. Mössbauer spectra of Sn^{119} impurity nuclei in nickel. The black dots correspond to $P = 1$ atm and the open circles to $P = 12.5$ kbar.

FIG. 2. Pressure dependence of $- \Delta H/H$ of Sn^{119} impurity nuclei in nickel; here, $\Delta H = H(P) - H(0)$.

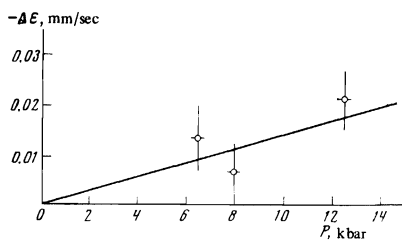FIG. 3. Pressure dependence of $-\Delta\varepsilon$ of Sn^{119} impurity nuclei in nickel.

FIG. 5. Pressure dependence of $\Delta H/H$ of Sn^{119} impurity nuclei in iron.

fine field is reduced by pressure, whereas the negative field increases in absolute magnitude.

3) The electron density in the vicinity of an Sn nucleus always decreases under pressure.

4) The value of $\Delta H/H\Delta P$ is largest for the Ni matrix in which the hyperfine field is smallest.

It is worth noting also that the isomeric shifts ε are approximately the same in all cases. This shows that the electron configurations of the Sn atoms are very similar in the two matrices.

We can easily see that the dependences $H(P)$ can be explained qualitatively by the model of "competing contributions."[8] According to this model, H can be expressed in the form

$$H = -H^{-}(r) + H^{+}(r). \tag{1}$$

where $H^{-}(r)$ and $H^{+}(r)$ are contributions to the field which are large in respect of their modulus (of the order of 1000 kG). These two contributions decrease with increasing distance r from a given localized magnetic moment to an atom of Sn. It is important to note that, in accordance with the model, [8] the dependence of $H^{-}(r)$ on the distance is much stronger than that of $H^{+}(r)$. Thus, when the distance between atoms is reduced under pressure, $H^{-}(r)$ should rise much more rapidly than $H^{+}(r)$. In other words, pressure should result in a relative increase of the negative contribution to the hyperfine fields, which is in full agreement with the experimental results. It is also clear that the value of $\Delta H/H\Delta P$ is largest in the case when the two
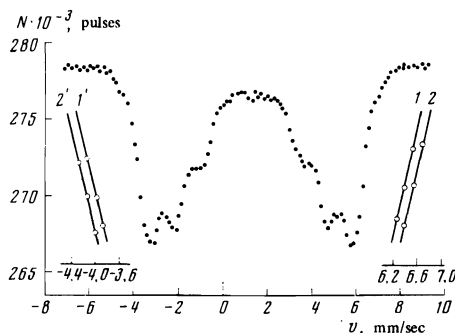

FIG. 4. Mössbauer spectrum of Sn^{119} nuclei in iron at $P=1$ atm. The straight lines represent the parts of the spectrum plotted on a larger velocity scale. The numbers 1 and 1' correspond to $P=1$ atm and the numbers 2 and 2' correspond to $P=10$ kbar.
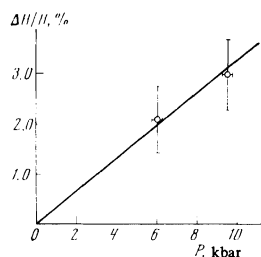
contributions to H almost cancel each other, i.e., when H is small. This is again in agreement with the experimental results. Unfortunately, the model in[8] does not predict the nature of the radial dependences of the contributions to H. However, if we make some assumptions about the radial dependences of $H^{-}(r)$ and $H^{+}(r)$, we can "match" this model quantitatively to the experimental results. We shall describe the field H by[8]

$$H = a\mu_1 + b\mu_2 + c\bar{\mu}, \tag{2}$$

where $a = -218$, $b = +9$, $c = +165$; μ_1 and μ_2 are the magnetic moments of the matrix atoms in the first and second coordination spheres of a Sn atom, respectively; $\bar{\mu}$ is the magnetic moment per matrix atom. In the first approximation, we can ignore the small coefficient b and assume that a, c, μ_1 and $\bar{\mu}$ are pressure-dependent. Then,

$$H \approx a(r)\mu_1(P) + c(r)\bar{\mu}(P). \tag{3}$$

It should be noted that the above expression reduces to Eq. (1) if we introduce $H^{-}(r) = -a(r)\mu_1(P)$ and $H^{+}(r) = c(r)\bar{\mu}(P)$. Using Eq. (3), we can obtain the experimental value of ΔH (for a given value of P) in the case of an Sn impurity in the iron matrix on the assumption that the radial dependences are $a(r) \propto r^{-3}$ and $c(r) \propto r^{-1}$; we have to use here the proportionality between $\mu_1(P)$, $\bar{\mu}(P)$, and $\sigma(P)$ and allow for the compressibility of iron as well as for the tabulated dependence $\sigma(P)$. The experimental data on the radial dependences of $H^{-}(r)$ and $H^{+}(r)$ can clearly be obtained by measuring $H(P)$ in those cases when one of the contributions to H predominates.

The results obtained allow us, with a high degree of certainty, to regard as incorrect the hypothesis that the positive contribution to H is due to the direct overlap of the wave functions of the magnetic electrons of the matrix atoms and of the outer electrons of the Sn atom. [14,15] In this case pressure should have increased the positive contribution to H, which contradicts the experimental results. The results of our studies show also that the models that do not assume the existence of two competing contributions to H fail to describe the real situation in metal systems. One should mention that usually the value of H of nonmagnetic atoms is regarded by analogy with the Knight shift and described by the formula

$$H = \frac{8\pi}{3}\mu_B\langle|\psi(0)|^2\rangle_F n\rho, \tag{4}$$

where $\langle|\psi(0)|^2\rangle_F$ is the probability density of s-like conduction electrons in the vicinity of a nucleus,

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averaged over the states on the Fermi surface; n is the number of electrons per unit cell of a nonmagnetic atom; ρ is the degree of polarization of these electrons; μ_B is the Bohr magneton. The measured isomeric shifts indicate that the electron density in the vicinity of an Sn nucleus is approximately the same in the cases discussed above. Moreover, the electron density decreases in all three systems under pressure. In accordance with Eq. (4), we would expect the absolute values of the fields to decrease in all cases, which is not in agreement with the experimental results. (We are allowing here for the fact that, in the range of pressures employed, the values of ρ also decrease proportionally to σ, whereas n remains practically constant.)

Thus, we may conclude that the dependences $H(P)$ can be explained if allowance is made for two contributions of opposite sign and with radial dependences. Moreover, the model of "competing contributions" explains qualitatively the experimental results. A fuller check of this model and its refinement would require new experimental data particularly on systems in which one of the contributions to the hyperfine field predominates over the other.

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Isotropic exchange interaction of pairs on Ni²⁺ ions in zinc fluorosilicate at high pressures

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The crystal resonator method was used in an ESR investigation of the dependences of the exchange integrals of Ni²⁺ ion pairs in ZnSiF₆·6H₂O single crystals on hydrostatic pressure. The investigation was carried out in the frequency ranges 24 and 72 GHz at temperatures of 1.6–4.2°K. A change in the isotropic exchange interaction was deduced from the high-pressure ESR spectra of exchange pairs recorded for various orientations of the magnetic field relative to the C₃ symmetry axis. The exchange integral of the nearest-neighbor Ni²⁺ ion pairs increased exponentially when the lattice constant was reduced by compression.

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1. INTRODUCTION

Investigation of the exchange interactions of impurity ion pairs in diamagnetic matrices provides one of the direct methods for the identification of the process of formation of exchange-coupled clusters in magnetic materials, determination of the magnetic structures of these clusters, and estimation of the adequacy of the description of local and macroscopic properties. Determination of the exchange integrals by the ESR method is now traditional. However, in the case of weakly coupled exchange pairs of Ni²⁺ ions in ZnSiF₆ · 6H₂O [1] the ESR method has made it possible to determine spectroscopically the exchange integrals. Therefore, a high-pressure investigation of the ESR spectra of Ni²⁺ exchange pairs in ZnSiF₆ · 6H₂O provides an opportunity for direct determination of the dependences of the exchange integrals on the interionic distances.

The ESR spectrum of exchange pairs is described under normal conditions by the spin Hamiltonian[1]

$$\mathcal{H}=g\beta H(S_1+S_2)+D(S_{1z}^2+S_{2z}^2)+J(S_1S_2), \qquad (1)$$

where the spectroscopic splitting factor is isotropic and equal to $g = 2.230 \pm 0.005$, D is the initial splitting of nickel ions in the trigonal field, $D = -0.134 \mp 0.005$ cm⁻¹, and J is the exchange integral of the isotropic interaction.

If a magnetic field H_0 is oriented parallel to the symmetry axis C_3, the eigenvalues and wave functions of the Hamiltonian (1) are found by diagonalizing it (see,