Mössbauer effect under pressure on tin impurity-atom nuclei in the alloys Pd-Fe and Pd-Co, and the hyperfine magnetic field model

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The Mössbauer effect under pressure at nuclei of tin impurity atoms in alloys of palladium with iron and cobalt is measured. The relative changes in the hyperfine fields $\Delta H/H\Delta p$ at ^{119}Sn are equal to $(-5.0\pm 1)\times 10^{-3}$ kbar^{-1} in the $Pd_{0.95}Fe_{0.05}$ matrix, $(-1.0\pm 0.2)\times 10^{-2}$ kbar^{-1} in the $Pd_{0.897}Co_{0.103}$ matrix, and $(-1.0\pm 0.4)\times 10^{-2}$ kbar^{-1} in the $Pd_{0.865}Fe_{0.135}$ matrix. The results agree with the model of "competing contributions." [2-4] An attempt is made to identify more concretely, within the framework of this model, the physical mechanisms whereby the fields H are formed. It is proposed that the negative contribution to H is due to spin polarization of the local charge ΔZ that screens the tin atom, while the positive contribution is due to polarization of the conduction electrons from remote coordination spheres of the tin atom. An anomalous increase of the probability of the Mössbauer effect on ^{119}Sn nuclei under pressure was observed.

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Hyperfine magnetic fields H, whose magnitudes and signs contain information on the spatial distribution of the spin density in magnetic crystals, are produced at the nuclei of impurity atoms dissolved in metallic magnetic matrices. It is impossible, however, to make full use of this information because the mechanism whereby the hyperfine fields are formed are unknown. The difficulties of this problem were formulated by us in[1], where we proposed to use investigations of the Mössbauer effect under pressure to bring to light the nature of H and, in particular, to determine their radial dependences. The results of[1] were qualitatively explained by means of the model of "competing contributions"[2-4]; this has revealed the inconsistency of the model,[5,6] according to which a positive contribution to H is due to direct overlap of the wave functions of the magnetic electrons of the matrix and of the outer electrons of the tin impurity atoms.

In the present study we undertook the following: first, to verify how general the regularities of the behavior of the field H at tin nuclei when a larger number of magnets is considered, and second, to specify more concretely the model of competing contributions.

We investigated H under pressure at the nuclei ^{119}Sn in alloys of palladium with iron and with cobalt. It is known that a distinguishing feature of these alloys is that at low concentrations of Fe(Co) the ferromagnetic interaction in these alloys is effected via the conduction electrons, and the palladium atoms "become magnetized" and acquire an average magnetic moment $\sim 0.09\mu_B$.[7] The choice of these substances is dictated also by the relatively large probability of the Mössbauer effect and by the possibility of varying the Curie temperature of the alloys by selecting the concentration of the iron or cobalt. We investigated *in passim* the probability of the Mössbauer effect on tin impurities, since no such experiments were performed earlier.

EXPERIMENT

Three alloys were prepared: $Pd_{0.897}Co_{0.103}$, $Pd_{0.805}Fe_{0.135}$, and $Pd_{0.95}Fe_{0.05}$. The Fe(Co) concentrations in the first two were chosen to make the alloys ferromagnetic at room temperature. The Fe concentration in the third alloy was relatively low, so that the iron could be regarded as diluted. We introduced into the alloys about 0.5 at.% of tin enriched with the isotope ^{119}Sn. The resonance spectra were measured on powdered absorbers 110 mg/cm^2 thick. In the low-temperature measurements, the high-pressure chamber was placed in a bath with liquid nitrogen. To determine the pressure at 78 K, the readings of the pressure sensors were corrected to take into account the temperature coefficients of the resistivity. In all other respects the technique of measuring the Mössbauer effect, of producing the hydrostatic pressures, and of the reduction of the resonance spectra was the same as in[1].

RESULTS AND THEIR DISCUSSION

1. Hyperfine magnetic fields

We measured first the Mössbauer spectra of all the samples at atmospheric pressure in a wide range of temperatures near the corresponding Curie temperatures (T_c). The spectra comprised single symmetrical lines (there was no splitting because of the small values of the hyperfine fields). From the formula $\Gamma = 0.14H + \Gamma_0$ [8] (where Γ and Γ_0 are the line widths in mm/sec and H is the field in kG) we obtained the temperature dependences $H(T)$. By extrapolating the steep sections of $H(T)$ to $H=0$ we determined the values of T_c, which agreed with the published data. The solid line in Fig. 1 is a plot of $H(T)$ for the alloy $Pd_{0.897}Co_{0.103}$, and is close to linear at $T<T_c$. The plots of $H(T)$ for the two other alloys were similar in form.

The solid lines of Fig. 2 show the experimental pres-

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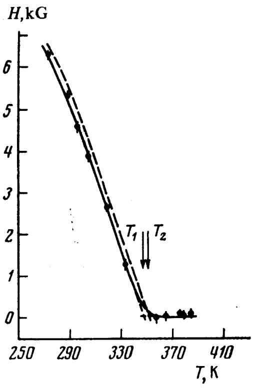

FIG. 1. Temperature dependence of the hyperfine magnetic field at ^{119}Sn nuclei in the alloy $Pd_{0.897}Co_{0.103}$. Solid curve—experiment, the dashed curve was obtained by parallel shift of the solid curve by an amount $\Delta T_c = T_c(p_2) - T_c(p_1)$. The arrows indicate the values of T_c at $p_1 = 0$ and $p_2 = 10$ kbar.

sure dependences of H for the alloys $Pd_{0.865}Fe_{0.135}$ and $Pd_{0.897}Co_{0.103}$ at room temperature and for the alloy $Pd_{0.95}Fe_{0.05}$ at 78 K. The error in H was determined mainly by the accuracy with which the spectrometer was calibrated, and was equal to $\sim \pm 0.1$ kG, while the error in the pressure measurements was determined by the manometer calibration accuracy and does not exceed the dimensions of the points on the plots.

The experimentally determined quantity $\Delta H_{exp} = H(p) - H(0)$ depends strongly on the proximity of the measurement temperature to the Curie temperature. The point is that H varies in the same manner as the magnetization σ, while σ is strongly altered by pressure in the region $T \approx T_c$. H therefore changes under pressure both as a result of the redistribution of the spin density in the crystal and as a result of the shift of T_c. The second effect is trivial in the sense that it carries no information on the spin-density redistribution of interest to us. Since $H(T)$ is a nearly linear function in the region of the measurement temperatures (see Fig. 1), we can, knowing $\Delta T_c/\Delta p$ "reconstruct" the form of $H_1(T)$ with only the $T_c(p)$ effect taken into account by a parallel shift of the $H(T)$ line by an amount ΔT_c corresponding to the pressure Δp. Thus, for the $Pd_{0.897}Co_{0.103}$ alloy we have $\Delta T_c/\Delta p = 0.27$ °K/kbar[9] and the "reconstructed" dependence at $p = 10$ kbar is shown in Fig. 1 by the dashed line. It was assumed that the $H(T)$ curves have the same shape without pressure and under pressure.

The dashed line of Fig. 2b shows the calculated plot of $H_1(p)$ that should be obtained as a result of the increase of T_c under pressure. The quantity of interest to us, which will henceforth be designated ΔH, and which reflects the change of the spin density, is the difference between the ordinates of the solid and dashed lines at a fixed pressure. This definition of ΔH excludes the influence of the pressure on T_c. For alloys of palladium with iron we have $\Delta T_c/\Delta p \approx 0$,[10] and therefore no corrections for the $T_c(p)$ effect were introduced in the determined values of H.

The data obtained from the reduction of the plots of Figs. 1 and 2 are gathered in Table I with the results of earlier studies.[1,11] Attention is called to the large values of the relative changes $\Delta H/H\Delta p$ for the palladium alloys. It is seen from the table that the values of ΔH in Pd-Fe and Pd-Co alloys are negative and decrease with decreasing $|H|$, while the values of $\Delta H/H\Delta p$ increase in absolute value with decreasing $|H|$. Thus, the behavior of H at the ^{119}Sn nuclei under pressure in alloys of palladium and in matrices of Co_2MnSn, Fe and Ni[1,11] agree qualitatively. The behavior of H in the dilute alloy $Pd_{0.95}Fe_{0.05}$ likewise exhibits no deviation from the general rule, despite the singularities of the exchange-mechanism interaction in this alloy. This means that the model of competing contributions[2-4] is applicable also to palladium alloys. According to this model

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

and $\Delta H = H(p) - H(0)$ should always be negative in view of the stronger coordinate dependence of $H^-(r)$ compared with $H^+(r)$ (here $H^-(r)$ and $H^+(r)$ are contributions of large absolute value and of opposite sign to the resultant field).

It must be emphasized that we have specially selected for the investigations of $H(p)$ matrices of metallic magnets with different types of exchange interaction: thus, Co_2MnSn is an alloy of the Geissler type, Fe and Ni are typical 3*d* metals, and the magnetic order in alloys of palladium with iron and with cobalt is effected via the conduction electrons. In all cases, the model of competing contributions predicts the $H(p)$ dependence correctly. Consequently, its formulation has a reliable physical meaning.

Unfortunately, however, this model does not give any concrete mechanism whereby the hyperfine fields are formed, and, in particular, does not predict the form of their radial dependences. We have therefore attempted to make this model more concrete in the sense of bringing to light the physical mechanisms of the individual contributions to H. The basis for this attempt were the data on the functions $H(p)$ and experimental facts obtained by other methods.

We assume that the hyperfine field H at the tin nuclei

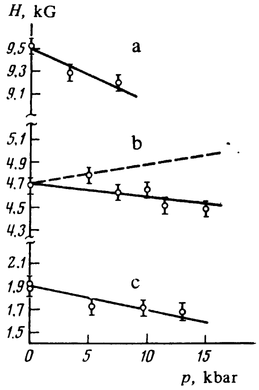

FIG. 2. Pressure dependences of the hyperfine fields at the nuclei ^{119}Sn: a—$Pd_{0.95}Fe_{0.05}$ at $T = 78$ K, b—$Pd_{0.897}Co_{0.103}$ at $T = 293$ K, c—$Pd_{0.865}Fe_{0.135}$ at $T = 293$ K. The dashed line shows the calculated $H_1(p)$ with account taken of only the influence of the pressure on T_c (see Fig. 1).

are the results of two types of spin polarization. The first type is local polarization of the electrons that screen the tin atoms. It is produced by the magnetic moments of the matrix atoms located in the first coordination sphere of the tin atom. The value of this polarization depends on the screening charge ΔZ and on the magnetic moment of the first coordination sphere. We assume also that this polarization makes a negative contribution to H via exchange polarization of the s electrons of the ion core of the tin atom. The second type is polarization of the conduction electrons, which oscillate in space and is damped with increasing distance from the tin atoms. The shape of the resultant oscillatory curve depends on the values and distribution of the magnetic moments of the matrix atoms over the coordination spheres. The polarization from the region of the first (and possibly second) sphere makes a negative contribution to H, while that from more remote spheres is positive. Thus, we rewrite expression (1) for H in the form

$$H=H^{-}_{\text{loc}}(r)+H_{\text{ce}}{}^{-}(r)+\sum_{i\geqslant 2} H^{+}_{i\,\text{ce}}(r), \tag{2}$$

where $H^{-}_{\text{log}}(r)$ is the negative contribution from the local screening charge ΔZ, $H^{-}_{\text{ce}}(r)$ is the negative contribution from the conduction electrons of the first (and second) coordination spheres, the last term in (2) takes into account the positive contribution from the conduction electrons from the third (second) and more remote spheres, and i is the number of the coordination sphere.

Let us discuss in greater detail these assumptions. It was shown experimentally in[13] that the polarization of the conduction electrons in an iron matrix oscillates with the coordinate, and the contribution to the resultant fields from the first two spheres is negative, while that from the more remote spheres is positive. This agrees with the Ruderman-Kittel-Kasuya-Yosida (RKKY) theory and is apparently a common property of metallic ferromagnets.[6] When an atom of a ferromagnetic matrix is replaced by the nonmagnetic tin atom, the distribution of the polarization far from the impurity atom changes little. Significant changes in the polarization take place near the tin atom, where the screening charge is concentrated. We propose that this polarization depends very strongly on the coordinates, since the charge ΔZ is localized on the Debye screening length, i.e., on distances on the order of the radius of the first coordination sphere. For the investigated matrices, ΔZ is practically constant. This is evidenced by the constancy of the isomeric shift δ of the Mössbauer spectra (see the table), which reflects the electron configuration of the tin atom. In other words, the tin atoms tend to preserve their "individuality" in the investigated metallic matrices. It appears that the contribution from the conduction-electron polarization is a relatively weak function of the coordinates, of the type $\sim r^{-3}$.

In addition to the model, let us consider the following singularity of the behavior of the tin atoms under pressure. In the immediate vicinity of the tin atom, the compressibility of the electron density can differ from the compressibility of the matrix. The point is that the compressibility of the alloy can be roughly estimated from the formula $K=\sum_i K_i C_i$, where K_i and C_i are the partial compressibilities and concentrations of the components. Since the compressibility of pure tin is approximately three times larger than the compressibility of the considered matrices, the increase of the resultant compressibility of the alloy with the tin can be due only to the larger compressibility of the tin. That this effect is possible in principle has been demonstrated theoretically[14] and experimentally[15]. Unfortunately, there are no published data on the compressibility of impurity tin in any matrix.

Let us verify now that with the aid of the proposed mechanisms of the formation of H we can qualitatively describe all the observed regularities in the behavior of H at the ^{119}Sn nuclei in metallic matrices under pressure. Let us list these regularities (see the table).

1) ΔH is always negative, regardless of the sign of H.

2) The relative changes of $\Delta H/H\Delta p$ are approximately one order of magnitude larger than the corresponding matrix compressibilities $\Delta V/V\Delta p$.

3) The ratios $\Delta H/H$ increase with decreasing absolute values of H.

4) the values of $\Delta H/H\Delta p$ are several times larger than the corresponding values of $\Delta\sigma/\sigma\Delta p$.

The first rule can be naturally attributed to the stronger radial dependence of the negative contribution in comparison with the positive contribution and to the larger compressibility of tin in comparison with that of the matrix. It appears that in experiments with pressure the principal role is always played by the increase of the negative contribution $H^{-}(r)$, in which $\Delta H<0$. The second rule seems quite surprising at first glance. Thus, for example, for tin in iron we have $\Delta H/H\Delta p \approx 6\Delta V/V\Delta p$. If we assume the compressibility K of the impurity tin atoms to be equal to the compressibility K_{Fe} of the iron matrix, then we obtain from this relation the unlikely radial dependence $H\sim r^{-18}$. This example shows that a comparison of the relative changes of the resultant field H and of the volume V is apparently incorrect. There are two reasons for this. First, the difference between the compressibilities of the impurity and the matrix. Thus, if we assume $K=K_{\text{Sn}}$, then $\Delta H/H\Delta p\approx 2\Delta V/V\Delta p$ and $H\sim r^{-6}$. Second, ΔH should be compared with H^{-}, and not with the resultant field $H=H^{-}+H^{+}$, the absolute value of which is much smaller than that of H^{-}. This point of view explains the second and third rules, that also makes it clear that at this stage it is impossible to use the connection between $\Delta H/H\Delta p$ and $\Delta V/V\Delta p$ for the determination of the radial dependences of the contributions. Nonetheless, the $H^{-}(r)$ dependence can be determined in principle by investigating under pressure the value of H at the ^{119}Sn nuclei in metallic antiferromagnetic matrices, where $H\equiv H^{-}$ because the average polarization of the conduction electrons is equal to zero. The fourth rule is also the consequence of the strong $H^{-}(r)$ dependence, since the value of $H^{-}(r)$ is more strongly influenced by the decrease of the distances between the tin atoms and the nearest mag-

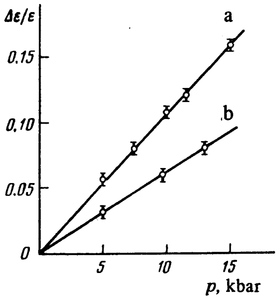

FIG. 3. Relative changes of the Mössbauer effect at the nuclei ^{119}Sn in palladium alloys under pressure at room temperature: a—$Pd_{0.897}Co_{0.103}$, b—$Pd_{0.865}Fe_{0.135}$.

netic matrix atoms than by the change in the magnetic moments (σ) themselves, which is proportional to the $\Delta V/V$ ratio of the matrix.

We note in conclusion that in a recent paper[16] an alternative model is proposed, in which, in contrast to the competing-contribution model, the field H is not resolved into components, and the influence of the screening charge on the polarization of the conduction electrons is introduced within the framework of the RKKY theory.

2. Probability of the Mössbauer effect

An anomalous increase of the Mössbauer effect was observed in the measured spectra of ^{119}Sn under pressure. This is shown in Fig. 3. The ratios $\Delta\varepsilon/\varepsilon$ at 10 kbar are respectively 0.06, 0.11, and 0.13 for the alloys $Pd_{0.865}Fe_{0.135}$, $Pd_{0.897}Co_{0.103}$, and $Pd_{0.95}Fe_{0.05}$. Since the line narrowing due to the decrease of H is only ~1% at 10 kbar, it can be assumed that $\Delta\varepsilon/\varepsilon \approx \Delta f'/f'$, where f' is the probability of the Mössbauer effect.

For Sn in metallic tin, the $f'(p)$ dependence was estimated in[17]. In the Debye approximation, the following expression was obtained for high temperatures ($T > \Theta$):

$$f'(p) = \exp\{-R/6kT - (V/V_0)^{2\gamma} Z_1(V_0)\}. \qquad (3)$$

Here R is the recoil energy, Θ is the Debye temperature, V_0 is the initial volume, V is the volume under pressure, γ is the Grüneisen constant, and $Z_1(V_0)$ is a factor that depends on Θ. To use this formula, it is necessary to know the value of $Z_1(V_0)$ under normal conditions. In the absence of pressure, the experimental value of f' for Sn in palladium agrees with that calculated by formula (3), provided that we introduce an effective Debye temperature $\Theta_{eff} = \Theta_{Pd}(m/M)^{1/2}$, where m and M are the masses of the impurity and matrix atoms.[18]

The question of the effect of pressure on f' of an impurity atom in a polyatomic unit cell has not been considered theoretically. We have estimated the changes of f' under pressure for the alloys by using formula (3) under the following rough assumptions: the Debye temperatures and the Grüneisen constants of the alloys are equal to the corresponding values for pure palladium, and the compressibility K of the impurity tin is equal to the compressibility K_{Pd} of pure palladium. The calculations yielded $\Delta f'/f' = 0.02$ at 10 kbar, which is much less than in our experiment. If we choose $K = K_{Sn}$ in place of $K = K_{Pd}$, then the calculation yields $\Delta f'/f' = 0.05$. This indicates that the rough estimates are unsatisfactory.

TABLE I. Experimental data on the hyperfine interaction for ^{119}Sn in the investigated magnetic matrices and certain characteristics of the matrices.

Matrix	Measurement temperature, °K	H, kG	δ, mm/sec	$\frac{\Delta H}{H\Delta p}\cdot 10^3$, kbar^{-1}	T_c, K	$\frac{\Delta\sigma}{\sigma\Delta p}\cdot 10^4$, kbar^{-1}	$K\cdot 10^4$, kbar^{-1}
Co_2MnSn [11]	293	97.6	1.40	−2±0.3	550	–	–
Fe [1]	293	−81.0	1.42	3±0.7	1043	−2.9 [12]	5.9
Ni [1]	293	18.6	1.47	−6.5±0.7	631	−2.4 [12]	4.9
$Pd_{0,95}Fe_{0,05}$	78	9.6	1.46	−5±1	178	–	5.3
$Pd_{0,897}Co_{0,103}$	293	4.7	1.48	−10±2	344	–	5.3
$Pd_{0.865}Fe_{0.135}$	293	2.0	1.50	−10±4	313	–	5.3

Note. Here H—hyperfine field, δ—isomeric shift relative to an SnO_2 source, T_c—Curie temperature, σ—magnetization, K—compressibility of matrix, $\Delta H = H(p) - H(0)$—change of field under pressure with allowance for the influence of the pressure on T_c (see the text).

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