Electric field gradient at ^{60}Co impurity nuclei in palladium hydrides

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The effect of hydrogen impurity on the orientation of ^{60}Co nuclei in a $Pd_{99}Co_1$ sample has been studied. It is suggested that a combination of a magnetic-dipole hyperfine interaction and an electric-quadrupole hyperfine interaction occurs in this system, with the axes of the electric field gradient distributed randomly with respect to the direction of the external magnetic field. A method described previously by Haroutunian *et al.* is used to calculate the electric field gradient. The gradients in two test samples, which were saturated with hydrogen in a gaseous medium at pressures of 4 Pa and $2.5 \cdot 10^4$ Pa, were found to be $2.6(6) \cdot 10^{19}$ V/cm^2 and $8.3(8) \cdot 10^{19}$ V/cm^2, respectively. The values found for the field gradient can be used to interpret the anomalous nuclear effects in deuterium-solid systems.

1. INTRODUCTION

Metallic palladium sorbs hydrogen well. The saturation of Pd with hydrogen is accompanied by corresponding changes in physical properties. The nuclear orientation of ^{60}Co in the polycrystalline alloy $Pd_{99}Co_1$ was studied in Ref. 1 as a function of the concentration of dissolved hydrogen. A significant decrease in the degree of nuclear orientation was observed when the alloy became saturated with hydrogen. This decrease was linked in Ref. 1 with changes in the magnetic properties alone of the palladium, caused by partial filling of the *d* band of metallic palladium by electrons of the sorbed hydrogen.

In this paper we examine another possible mechanism for suppression of the nuclear orientation. This mechanism is associated with the appearance of the electric quadrupole interaction of ^{60}Co as the result of disruption of the cubic symmetry of the crystal lattice of metallic palladium as it becomes saturated with hydrogen.

In the fcc lattice of palladium, hydrogen occupies octahedral interstitial positions.[2] Palladium hydride forms two phases, depending on the hydrogen concentration. These two phases have the structure of an isotropically expanded cubic lattice of the palladium matrix. The absorption of hydrogen to a concentration H/Pd$\leqslant$0.008 (the α phase) results in a gradual increase in the lattice constant from 3.891 to 3.894 Å. With a further increase in the hydrogen content, the β phase appears, with a local concentration H/Pd = 0.607. The lattice constant jumps abruptly to 4.026 Å. When the total hydrogen content reaches 0.607 throughout the entire volume, the α phase disappears. At concentrations between 0.008 and 0.607, the two phases coexist. This coexistence of two phases with different lattice constants results in the appearance of local deviations from cubic symmetry. Since the electric field gradient is zero at the sites of the cubic lattice, only the magnetic hyperfine interaction can occur in pure palladium and in the pure α and β phases. At intermediate hydrogen concentrations, however, the deviation from cubic symmetry may result in the appearance of a nonzero field gradient at the nucleus of an impurity Co atom. In this case the nuclear orientation of ^{60}Co in the $Pd_{99}Co_1$ (H) matrix should be thought of as the result of a combined interaction: the magnetic-dipole hyperfine interaction along with the electric-quadrupole hyperfine interaction.

Our purposes in the present study were to evaluate the quadrupole interaction of ^{60}Co from measurements of the low-temperature nuclear orientation in the matrix $Pd_{99}Co_1$ (H) and to determine the electric field gradient at a Co site.

2. ORIENTATION OF NUCLEI IN THE CASE OF A COMBINED INTERACTION

The quantity which is observed in experiments on nuclear orientation is usually the anisotropy of the angular distribution of γ rays:

$$W(\theta, T) = 1 + \sum_{k=2,4} A_k Q_k B_k(T) P_k(\cos\theta). \qquad (1)$$

The parameters A_k are determined by the nuclear decay scheme: Q_k are geometric factors which depend on the solid angle of the detector; P_k (cos θ) are the Legendre polynomials; θ is the angle between the γ emission direction and the quantization axis; and the orientation functions $B_k(T)$ are determined by the ratio of the splitting energy of the nuclear sublevels to the thermal energy, kT. If a magnetic field and an electric field gradient are acting on the nucleus, the interaction Hamiltonian determining the splitting energy can be written as the sum

$$H = H_e + H_m. \qquad (2)$$

If the orientation of the nuclei is caused by the magnetic

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hyperfine interaction, the quantization axis is the direction of the external magnetic field. In this case the functions B_k are determined by the parameter of the magnetic hyperfine splitting, $g\mu_n B/IkT$ (g is the g-factor of the nucleus, I is its spin, B is the magnetic field at the nucleus, and μ_n is the nuclear magneton).

In the case under consideration here, when the α and β phases coexist in palladium hydride, the electric field gradient at the Co nuclei may change in magnitude and direction from one lattice cell to another. Let us assume for simplicity that the field gradient has the same magnitude at each ^{60}Co nucleus and has axial symmetry. Haroutunian *et al.*[3] have offered a general expression for the angular distribution of the emission by the nucleus in the case of a combined interaction, if the axes of the electric field gradient are directed randomly with respect to the direction of the magnetic field. They showed that the effect of the quadrupole interaction can be reduced to multiplication of the orientation parameters B_2 and B_4 for the purely magnetic interaction by attenuation coefficients G_2 and G_4 which depend on the ratio of the contributions of the electric and magnetic interactions, $\hbar\omega_q$ and $\hbar\omega_B$. In this case the anisotropy of the angular distribution is

$$W(\theta, T)=1+\sum_{k=2,4} A_k Q_k G_k(\hbar\omega_q/\hbar\omega_B) B_k(T) P_k(\cos\theta). \tag{3}$$

In this paper we calculate the attenuation coefficients for the spin of the ^{60}Co nucleus, $I=5$, and for various values of the ratio of the electric and magnetic interactions. The procedure for calculating G_2 and G_4 is similar to that described in Ref. 3.

We direct the z axis of the laboratory coordinate system along the external magnetic field B. We denote the eigenvectors of the operators I_z and I^2 in this coordinate system by $|m\rangle$. For each lattice cell which contains an impurity ^{60}Co nucleus, we choose a corresponding local coordinate system, with the z' axis along the axis of the electric field gradient at the ^{60}Co nucleus. The eigenvectors of the operators $I_{z'}$ and I^2 in the local coordinate system are denoted by $|N\rangle$. The matrix elements of the Hamiltonian (2) in the laboratory coordinate system are

$$\langle m|H|m'\rangle=-g\mu_n B m\delta_{mm'}+\langle m|H_e|m'\rangle. \tag{4}$$

Under the condition that axial symmetry prevails in this local coordinate system, the electric quadrupole interaction is described by the well-known expression

$$H_e=\frac{eQV_{zz}}{4I(2I-1)}[3I_{z'}^2-I(I+1)], \tag{5}$$

where Q is the quadrupole moment of the nucleus, and V_{zz} is the magnitude of the electric field gradient at the nucleus.

Using the elements $d^I_{mm}(\alpha\beta\gamma)$ of the finite-rotation matrix (α, β, and γ are the usual Euler angles), we can relate the laboratory and local coordinate systems. Haroutunian *et al.*[3] showed that the eigenvalues of the Hamiltonian H depend only on the angle β between the z and z' axes. Introducing

$$\hbar\omega_q=eQV_{zz}/4I(2I-1), \tag{6}$$

$$\hbar\omega_B=g\mu_n B, \tag{7}$$

we can show that the matrix of the overall Hamiltonian is

$$\langle m|H|m'\rangle=\hbar\omega_B\left\{-m\delta_{mm'}+\frac{\omega_q}{\omega_B}\sum_\mu d^I_{m\mu}(\beta)d^I_{m'\mu}(\beta)[3\mu^2-I(I+1)]\right\}. \tag{8}$$

Diagonalizing this matrix, we find the eigenvalues E_N and the eigenvectors $|N\rangle$ of the oriented state in those local coordinate systems for which the z' axis makes an angle β with the z axis of the laboratory coordinate system. These eigenenergies and eigenvectors depend on ω_q and ω_B. We can then construct the density matrix for the nuclear ensemble in these local coordinate systems:

$$\langle N|\rho|N'\rangle=\frac{\exp(-E_N/kT)}{\sum_{N''}\exp(-E_{N''}/kT)}\delta_{NN'}. \tag{9}$$

Using the basis vectors $|m\rangle$, we can write an expression for this density matrix in the laboratory coordinate system:

$$\langle m|\rho|m'\rangle=\sum_{N,N'}\langle m|N\rangle\langle N|\rho|N'\rangle\langle N'|m'\rangle. \tag{10}$$

Having found the density matrix (10), we can calculate the values of the orientation parameters from the known expression[4]

$$B_k(\beta, \omega_q, \omega_B)=[(2k+1)(2I+1)]^{1/2}\times\sum_m(-1)^{I+m}\begin{pmatrix} I & I & k\\ -m & m' & 0\end{pmatrix}\langle m|\rho|m'\rangle\delta_{mm'}. \tag{11}$$

Since the electric field gradient has a random spatial direction in our case, it is necessary to integrate B_2 and B_4 over all the local coordinate systems, i.e., over all Euler angles. The orientation parameters describing the state of the entire ensemble of ^{60}Co nuclei are then

$$\bar{B}_k=\int B_k(\beta, \omega_q, \omega_B)\sin\beta\, d\beta. \tag{12}$$

We introduce attenuation coefficients as the ratios

$$G_k(\hbar\omega_B/kT, \omega_q/\omega_B)=\frac{\bar{B}_k(\hbar\omega_B/kT, \omega_q/\omega_B)}{B_k(\hbar\omega_B/kT)}, \tag{13}$$

where B_k are the nuclear-orientation parameters for the case of a magnetic interaction. Figure 1 illustrates the situation with a plot of the attenuation coefficients G_2 and G_4 calculated in this fashion as a function of the ratio $3\omega_q/\omega_B$ at a temperature of 15.3 mK.

Using the measured anisotropy of the angular distribution, $W(T)$, and using expression (3) for an approximation, we can derive the magnitude of the electric quadrupole inter-

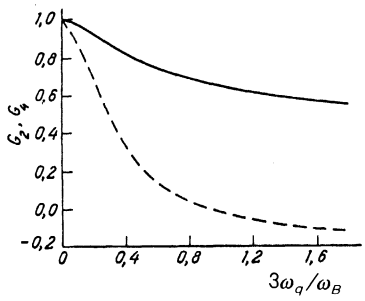

FIG. 1. Attenuation coefficients G_2 (solid line) and G_4 (dashed line) as a function of the ratio $3\omega_q/\omega_B$ at a temperature of 15.3 mK.

action in a comparatively simple way if the magnitude of the magnetic hyperfine interaction is known.

3. DETERMINATION OF THE ELECTRIC FIELD GRADIENT AT ^{60}Co IN PALLADIUM HYDRIDE

Let us examine the experimental data. The temperature dependence of the angular anisotropy of the γ emission of ^{60}Co nuclei oriented in a ferromagnetic $Pd_{99}Co_1$ matrix was measured in Ref. 1 at low temperatures in an external field of 1.2 T. A total of three samples were studied. Two of them were held in purified hydrogen at a pressure ≈ 4 Pa (sample I) or $2.5 \cdot 10^4$ Pa (sample II). A sample which had been annealed in vacuum at 800 °C just before the orientation measurements was used as a control sample (III). The temperature was measured with a ^{54}MnNi nuclear thermometer.

Figure 2 shows the temperature dependence of the angular anisotropy measured for samples I–III. For sample III, for which the nuclear polarization was caused exclusively by the magnetic hyperfine interaction, we find the magnetic hyperfine field at ^{60}Co to be $B_{\rm hf} = 21.6(5)$ T. This figure agrees well with results measured by an NMR method.[5] For hydrogen-saturated samples I and II, the values of the anisotropy are lower than that of the control sample, and

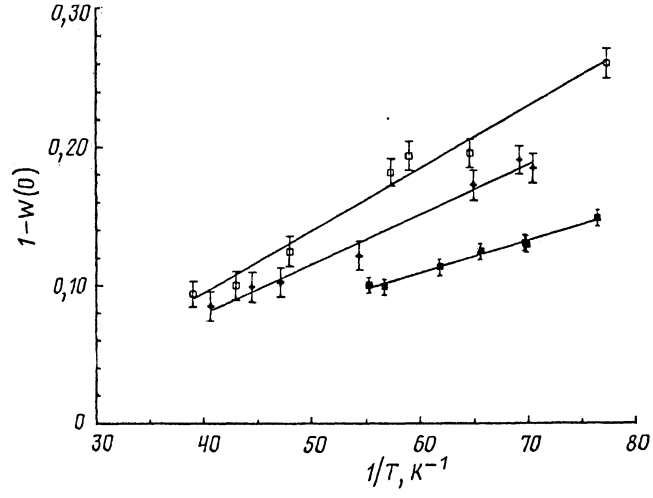

FIG. 2. Temperature dependence of the γ anisotropy of oriented ^{60}Co nuclei in $Pd_{99}Co_1$. + —Sample saturated with hydrogen at a pressure of 4 Pa; ■—the same, but at a pressure of $2.5 \cdot 10^4$ Pa; □—sample annealed in vacuum.

there is an obvious dependence on the amount of hydrogen in the sample.

The experimental results found for samples I and II were analyzed under the assumption that the ^{60}Co nuclei experience the resultant effect of the magnetic hyperfine field $B_{\rm hf}$ mentioned above and the randomly oriented field gradient. Expression (3) can be used to write the following equation for each experimental point on the plot of $W_i^{\rm exp}(T_i)$:

$$W_i^{exp} = 1 - 0{,}40794 B_2 (B_{hf}/T_i) G_2 (\hbar\omega_q/\hbar\omega_B, T_i) - 0{,}21913 B_4 (B_{hf}/T_i) G_4 (\hbar\omega_q/\hbar\omega_B, T_i). \quad (14)$$

The Legendre polynomials P_2 and P_4 equal unity in this case, since the measurements were carried out at an angle $\theta = 0°$. The magnetic-interaction parameter $\hbar\omega_B$ for the given $B_{\rm hf}$ was calculated from (7). Accordingly, the only unknown in (14) is the parameter of the electric quadrupole interaction, $\hbar\omega_q$. [Using expression (6), we find that Eq. (14) has one unknown: V_{zz}, the electric field gradient.] Since the attenuation coefficients G_2 and G_4 are monotonic functions of $\hbar\omega_q$, we can use a method of successive iterations to solve Eq. (14). In each iteration, an intermediate value of $\hbar\omega_q$ makes it possible to find G_2 and G_4 by the method described above. These values are then substituted into Eq. (14). This procedure of approaching $W_i^{\rm exp}$ is repeated until the difference between the right and left sides of (14) becomes much smaller than the experimental error. Using the values found for $\hbar\omega_q$ and (6), we find the values of the electric field gradient. Here we use the known value[6] of the quadrupole moment of the ^{60}Co nucleus: $Q = 0.44$ b. Figure 3 shows the electric field gradients calculated in this manner for the corresponding experimental points in Fig. 2. As expected, the electric field gradient is independent of the temperature, to the accuracy of the calculation.

Table I shows values of the electric field gradient averaged over all the experimental points.

The values found for the electric field gradient in this manner are considerably higher than the values customarily found for regular lattices of noncubic metals.[7] On the other hand, such high values of the gradient are not unique. For example, Marest *et al.*[8] found $V_{zz} = 2.8 \cdot 10^{20}$ V/cm^2 for a Y

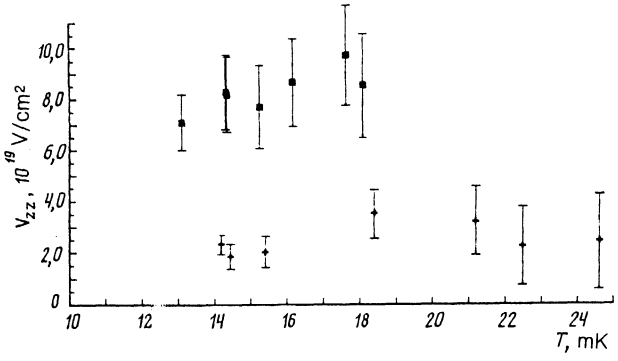

FIG. 3. Calculated values of the electric field gradient for the experimental points. The notation is the same as in Fig. 2.

TABLE I.

Sample	Saturation with hydrogen at pressure, Pa	Gradient, V/cm^2
I	4	$2,6(6)\cdot 10^{19}$
II	$2,5\cdot 10^4$	$8,3(3)\cdot 10^{19}$

impurity in a cubic Al crystal. They believe that absorbed oxygen was responsible for that value. The pronounced weakening of the anisotropy observed by Brewer and Kopp[9] in ^{95}NbCu—the authors attributed the effect to the formation of hydrides—can be explained by the presence of an electric field gradient of the same order of magnitude or even higher.[8]

4. CONCLUSION

Research on the properties of palladium hydrides has recently been spurred by the detection of anomalous nuclear effects (e.g., the emission of neutrons) in deuterium-solid systems. Efforts to explain these effects have invoked (in particular) the idea that deuterons are accelerated by the electric fields in the crystals. The accelerating potential required to effectively penetrate the Coulomb barrier when two deuterons coalesce has been estimated to be 10^3–10^4 V (Ref. 10). Such fields are usually regarded as being generated by electric charges which arise along the edges of cracks which form during the hydrogenation. The estimates of the electric field gradient in palladium hydride found in the present study may indicate the existence of electric fields on this order of magnitude within one lattice constant (3–4 Å). In contrast with the crack mechanism, in which the electric field should decrease rapidly as a result of a leakage of charge in a metal, the field should not vary rapidly in time in the case under consideration here.

[1]G. M. Gurevich, A. L. Erzinkyan, P. Malinskiĭ *et al.*, Izv. Akad. Nauk SSSR, Ser. Fiz. **50**, 2328 (1986).
[2]G. Alefeld and J. Voelkl (eds.), *Hydrogen in Metals*, Springer–Verlag, New York, 1978 (Russ. trans., Mir, Moscow, 1981).
[3]R. Haroutunian, M. Meyer, and R. Coussement, Phys. Rev. C **17**, 292 (1978).
[4]K. S. Krane, Data Tables **11**, 407 (1973).
[5]M. Katayama, K. Kumagai, T. Kohara *et al.*, J. Phys. Soc. Jpn. **40**, 429 (1976).
[6]C. M. Lederer and V. S. Shirley (eds.), *Tables of Isotopes*, Wiley-Interscience, New York, 1978.
[7]E. Hagn, Hyperfine Interact. **22**, 19 (1985).
[8]G. Marest, R. Haroutunian, and I. Berkes, Phys. Rev. C **17**, 287 (1978).
[9]W. Brewer and M. Kopp, Hyperfine Interact. **2**, 299 (1976).
[10]V. A. Tsarev, Usp. Fiz. Nauk **160**(11), 1 (1990) [Sov. Phys. Usp. **33**(11), 881 (1990)].

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