ISOMER SHIFTS ON Sn^{119} IMPURITY NUCLEI IN Pd-H ALLOYS

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The dependences of the isomer shift of Sn^{119} impurity nuclei on the component concentration in Pd–H and Pd–Ag binary alloys are studied. The lattice constants of the Pd–H alloy phases are practically independent of the hydrogen concentration. The curves were found to be similar, whence it is concluded that for the alloys investigated the isomer shift on Sn^{119} impurity nuclei does not depend strongly on the differences between the atomic radii. An attempt is made to estimate the change in the isomer shift on Sn^{119} impurity nuclei with a filled 5s state of the impurity atom.

THE investigation of isomer shifts on Mössbauer nuclei in alloys is of considerable interest from the point of view of the study of the behavior of the valence electrons of the components of the alloy. A considerable amount of data is at present available on the isomer shifts for binary systems where the Mössbauer effect can be observed for the nuclei of one of the components. The detailed interpretation of the dependences of the isomer shift on the composition of the alloy and a comparison of the data for various alloys are made difficult by the presence in real compounds of different forms of the chemical bond, and hence by possible changes of the atomic volume of the Mössbauer atom on alloying.

The investigation of the electronic properties of various alloys when using stable Mössbauer impurity atoms is connected with the necessity of introducing the assumption that the effect of a rather appreciable amount of impurity atoms (~ 1 at.%) on the basic properties of the matrix is negligibly small and that the electron configuration of the ionic core of the impurity atoms remains constant with changing alloy composition, which is in general not obvious.

In order to study further the nature of the isomer shift, in particular the effect of the atomic volume, we measured the isomer shifts on Sn^{119} impurity nuclei in Pd–H alloys. It is known[1] that the properties of palladium alloys are well described by the rigid-band model; it is usually assumed that the valence electrons of the impurity fill mainly the d band of palladium. This refers also to the palladium-hydrogen alloys in which the solubility of the latter reaches 60 at.%. Hydrogen is a penetration impurity and the Pd–H alloys are

two-phase alloys. One phase is almost pure palladium, whereas the composition of the other is described approximately by the formula PdH$_{0.6}$. The lattice parameters of the two phases are practically independent of the hydrogen concentration up to a hydrogen content of the order of 60 at.%.[2]

This is also observed in dissolving hydrogen in palladium alloys with ten percent copper and in alloys of the Pd–Ag system.[3] It turns out that on being alloyed with palladium silver behaves in the same way as hydrogen.[3] Thus, using the data on the identical behavior of hydrogen and silver in alloys with palladium, one can attempt to determine the effect of a change of the lattice constant on the magnitude of the isomer shift in the case of an impurity atom, as well as the admissibility of the assumption that it is possible to investigate the electronic properties of alloys after the introduction of an appreciable amount (~ 1 at.%) of Mössbauer impurity atoms.

The concentration of tin impurity atoms was 1.4 at.%; the tin used was enriched with the Sn^{119} isotope to 66.3% and the purity of the palladium was no worse than 99.99%. Arc melting in an argon atmosphere was used to alloy the tin and the palladium. After the alloying, the sample underwent homogenizing annealing in a helium atmosphere at 700–800° C for 80 hours. A 0.1-mm foil was then prepared from the alloy; the rolling was followed by annealing to relax the strains.

A foil of metallic tin served as the source of resonance γ radiation. In the course of the measurements the source and the absorber were at liquid nitrogen temperature. The resonance absorption spectra were obtained on a setup with mechanical drive.

The hydrogenation of the sample proceeded by placing it into gaseous hydrogen at normal pressure, prolonged heating at 180°C, and subsequent slow cooling together with the furnace. The sample was then kept at room temperature in a hydrogen atmosphere for a number of days. The amount of dissolved hydrogen was determined by weighing the sample before and after measuring the isomer shift. The weight of the sample after the measurement remained practically unchanged. The hydrogen was removed from the sample by heating in vacuum at 350°C. All measurements were carried out on the same sample.

The isomer shifts were determined from the difference in the number of counts at speeds corresponding to the maximum value of the derivative of the absorption line,[4, 5] and were also checked by determining its center of gravity.

The absorption spectra were in all cases symmetrical singlet lines (Fig. 1). Although, as was noted above, the sample should contain two phases after hydrogenation, the ratio of the phases depending on the hydrogen content, no splitting of the lines, asymmetry, or appreciable dependence of the line width on hydrogen concentration was noted.

Figure 2 shows the dependences of the isomer shift on Sn^{119} impurity nuclei in the Pd–H and Pd–Ag systems. In the latter case we only refined the course of the curve in the range of small silver concentrations and used further the data of Bryukhanov, Delyagin, and Shpinel'.[6] The magnitude of the isomer shift of the unhydrogenated sample coincided practically with the value of the shift for the Pd–Sn alloy with a small tin content.[7] In calculating the hydrogen concentration it was assumed that the hydrogen is in the alloy in the form of protons. Figure 2 shows that both curves are close to each other, the difference exceeding only slightly the experimental error. Tak-
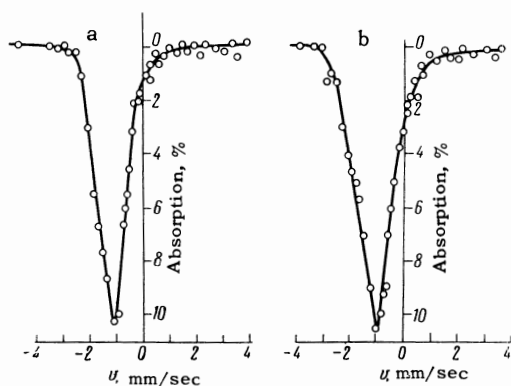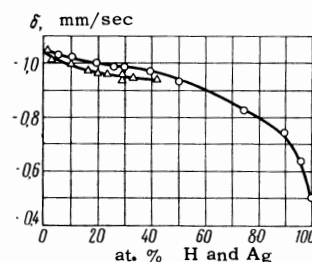

FIG. 2. Isomer shifts on Sn^{119} impurity nuclei in the Pd–H (Δ) and Pd–Ag (O) systems relative to a metallic Sn^{119m} source.

ing into account the experimental data on the identical behavior of silver and hydrogen alloyed with palladium,[3] we conclude that, notwithstanding the considerable difference of the atomic radii of silver and hydrogen, there is no essential difference in the isomer shifts for equal concentrations of these elements.

An analogous conclusion about the small role of the size factor can be reached from data on the Knight shift on vanadium and niobium nuclei in the V–A, V–Cr, Nb–H, Nb–Mo, and Nb–Tc systems, where the properties of the alloys are also well described by the rigid-band model and where it is assumed that on alloying the valence electrons of the impurity fill mainly the d band of the vanadium or niobium.[8] Also, notwithstanding the difference in the atomic radii of hydrogen and chromium, and also of hydrogen, molybdenum, and technetium, the concentration dependences of the Knight shifts practically coincide.

It appears thus that the change in the lattice constant as a function of the alloy content may not be of decisive importance in determining the magnitude of the isomer shift on the Mössbauer impurity nucleus. This conclusion is also supported by the symmetry of the singlet absorption line on the impurity nucleus in Pd–H alloys where there is the possibility of the presence of two phases with lattice parameters differing by a factor of 1.04.[2, 9]

The course of the isomer shift curve for the Pd–H system can be explained by an increase in the alloy of the fraction of the $PdH_{0.6}$ phase whose isomer shift differs little from the magnitude of the shift of the hydrogen-poor phase. The small difference in the shift for both phases can be related to the inappreciable effect of hydrogen on the nature of the interaction of the tin impurity nuclei with the palladium.

One can attempt to estimate the magnitude of the change of the isomer shift on filling one 5s state from the course of the curve of the isomer shift for the Pd–H system. If it is assumed that

FIG. 1. Absorption spectra on Sn^{119} impurity nuclei in the Pd–H system: a—unhydrogenated sample, b—sample with a hydrogen concentration of ≈42 at. %.

the tin impurity gives up its 5s and 5p valence electrons mainly to the d band of palladium, as was assumed in explaining the isomer shifts on the Sn[119] impurity nuclei,[10] then the screening of impurity atoms in compounds of the Pd–Sn system[11] is due to the electrons of the 4d band of palladium.[1] Since the 4d band of palladium is almost filled, the degree of screening should remain approximately constant on changing the concentration of conduction electrons due to the solution of hydrogen.[11] Thus the change in the isomer shift on the tin impurity should be due to the filling of its s states on increasing the concentration of conduction electrons, if we neglect the change in the character of the interaction of the tin and palladium atoms upon the solution of hydrogen, which screens by the action of the 5p electrons of tin its 5s electrons and the sd hybridization. Thus, whereas the introduction of 0.4 of an electron into the 4d and 5s band of palladium leads to a change in the isomer shift of 0.1 mm/sec, the filling of one state in the s shell of the tin impurity at the expense of the conduction electrons corresponds to an increase of 2.5 mm/sec in the isomer shift, which practically coincides with previous estimates.[12]

It should be noted that the approximately identical course of the curves of the isomer shift on the tin impurity in Pd–H and Pd–Ag alloys provides at most only evidence of the approximately identical behavior of the tin impurity in these alloys, and the question of the extent to which the tin impurity "follows" the change in the electronic properties of the alloy remains open.

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