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INVESTIGATION OF THE MÖSSBAUER EFFECT IN Pd-Sn *ALLOYS*

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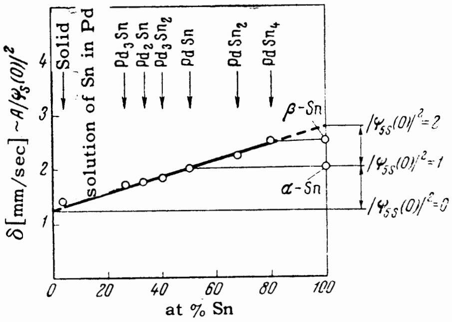
Isomer shifts in compounds of the Pd-Sn system were studied using resonance absorption of γ quanta. The effective number of s electrons in white tin is estimated.

UP to now the studies of resonance absorption of γ quanta have been done either on isolated compounds or over a limited range of solid solutions, which did not allow a study of the dependence of isomeric chemical shifts on atomic concentration of one of the components of the binary system. In the present work a complete study of the Pd-Sn system was made in order to see the influence of electron concentration on chemical shift during variation of the concentration of one of the alloy components. The following compounds in this system were studied: Pd_3Sn, Pd_2Sn, Pd_3Sn_2, PdSn, $PdSn_2$, $PdSn_4$, as well as the solid solution of tin in palladium up to 9.5 at. % Sn.

All the compounds were prepared by melting palladium with tin in quartz ampoules in vacuum. After heat treatment of the alloys in accordance with the phase diagram, the phase composition was studied using x ray analysis. Computation of the Debye pattern showed good agreement of the x ray phase parameters with the literature data.[1] To study the Mössbauer effect, absorbers with a 10 mg/cm^2 thickness in tin were prepared. The measurements were made on an apparatus giving a constant velocity of the absorber relative to the source. The source of the 23.8-keV γ quanta emitted from Sn^{119m} was a tin dioxide sample of thickness 5 mg/cm^2. The source was kept at room temperature for all measurements, while the absorbers were cooled to liquid nitrogen temperature. Radiation passing through the absorber was detected by a scintillation spectrometer with a flat NaI(Tl) crystal.

The resonance absorption spectra of the compounds of the Pd-Sn system showed no peculiarities and consisted of single lines of different width. The maximum of the absorption line was at positive velocities relative to the source. The figure shows the dependence on concentration of Sn for the isomeric chemical shift δ in compounds of the Pd-Sn system. Despite the fact that the compounds studied have different crystal structures, this dependence is linear up to the compound $PdSn_4$ which is richest in tin. The data on the isomeric shift for a solid solution of tin in palladium, found by Bryukhanov et al,[2] also fit on the straight line.



Dependence of isomeric shifts on atomic concentration of tin for the 23.8-keV transition of Sn^{119} in compounds of the Pd-Sn system. Shifts measured at room temperature relative to the γ transition in SnO_2.

It is known that the chemical shift δ is proportional to the electron density $|\psi_S(0)|^2$ at the origin of the Mössbauer atom, so we must assume that the linear dependence $\delta(c)$ (where c is the atomic concentration of tin) is related to the linear increase of electron density at the tin nucleus from some finite value at low tin concentrations up to a maximum of 100 at. % Sn in β-Sn. The change in $|\psi_S(0)|^2$ may occur mainly from a redistribution of the four valence electrons which form a $5sp^3$ hybrid for the equivalent covalent bonds in grey tin. Palladium is a transition metal and has an almost completely filled 4d band (9.4 electrons per atom); the 5s band, with an isoenergetic surface which is almost spherical, has 0.6 electrons per atom.[3] There are no reliable data on the effect of d electrons on the Fermi surface, but the d electrons seem to give only a small contribution to the transfer process. We may assume that for compounds of the Pd-Sn system the filling of the d band with increasing concentration of tin will not occur because of the s electrons of the palladium but because of the valence electrons from the tin, which go into the conduction band of the alloy. Such a shift of the tin valence electrons obviously results in a reduction of the electron density at the origin of the tin atoms. At high concentrations of palladium (solid solution of tin in palladium), this "siphoning off" is a maximum and $|\psi_{5S}(0)|^2$ (only for the 5s electrons of the tin, of course) becomes zero. Then as the tin atom concentration increases and the d band of palladium is being filled, the total number of electrons localized in 5s states of tin begins to increase, which results in compounds showing a definite effect on the chemical binding of the tin.

A comparison of the isomeric chemical shifts for PdSn with those for tin shows that there is the same shift for PdSn (50 at. % Sn) and for α-Sn, and since grey tin has one electron in the 5s shell, there should also be the same "effective" electron concentration at the tin nucleus in PdSn. From the figure we see that at a concentration of 50 at. % Sn there is an inversion point, and the normalization given above for this point gives $|\psi_{5S}(0)|^2 = 1$. Continuing the straight line $\delta(c)$ until it intersects the ordinate axis at 0 and 100% Sn, we get the surprisingly reasonable values $|\psi_{5S}(0)|^2 = 0$ for 0 at. % Sn (there are no electrons in the 5s shell of tin, since they have shifted into the conduction band) and $|\psi_{5S}(0)|^2 = 2$ for 100 at. % Sn (corresponding to the maximum number of electrons in the tin 5s shell). Such a normalization gives a possible estimate of the effective number of electrons in the 5s state of tin in the compounds: for white tin we get $|\psi_{5S}(0)|^2 = 1.67$ electrons per atom, which is close to the value found in[4] (1.5 electrons in the 5s state of tin).

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[3] Hoare, Matthews and Walling, Proc. Roy. Soc. (London) **A216**, 502 (1953).

[4] Bryukhanov, Delyagin, Kuz'min and Shpinel', JETP **46**, 1996 (1964), Soviet Phys. JETP **19**, 1344 (1964).

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