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The interaction between rhodium and impurity atoms of s–p elements dissolved in palladium

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Abstract. The perturbed angular correlation measurements were performed with ⁹⁹Rh in dilute PdX (X ≡ Cd, In, Sn, Sb) alloys and with ¹¹¹In in dilute Pd–Rh alloy. The rhodium atoms attract Cd, In, Sn and Sb impurities and impurity pairs of Rh–Cd, Rh–In, Rh–Sn and Rh–Sb are formed in a Pd matrix. Their binding energy was derived from the impurity pair concentration measured as the function of temperature. The negative binding energy contradicts the repulsive interaction predicted for those impurities by the semi-empirical model developed in the literature.

1. Introduction

The interaction between impurity atoms of two distinct elements in dilute ternary alloys has been the subject of numerous experimental studies in the last few years [1–3]. It was shown that the introduction of a trace element C into a dilute solid solution AB leads to an interaction between C and B atoms and consequently to their non-random distribution over the lattice sites. The attractive or repulsive interaction between them causes the relative concentration of nearest-neighbour pairs of two different impurities to be higher or lower respectively than it would be for the statistical distribution of the individual constituents.

Evidence for the impurity pair interaction can be easily obtained with hyperfine interaction techniques such as nuclear magnetic resonance, the Mössbauer effect and perturbed angular correlation (PAC). In particular, PAC spectroscopy has several features, such as the ability to deal with very low impurity concentrations as well as to perform experiments without restriction in temperature, which make it especially suitable for alloy studies. A specific PAC radioactive probe of extremely low concentration (about 10^{-8}) introduced into a dilute binary alloy is sensitive to its local environment and it monitors the occupation of its nearest-neighbour sites by the minor constituent of the alloy. From the temperature dependence of the nearest-neighbour probe–impurity pair number, one can draw conclusions about the energy involved in the impurity pair interaction and about the entropy of formation for such two atom complex.

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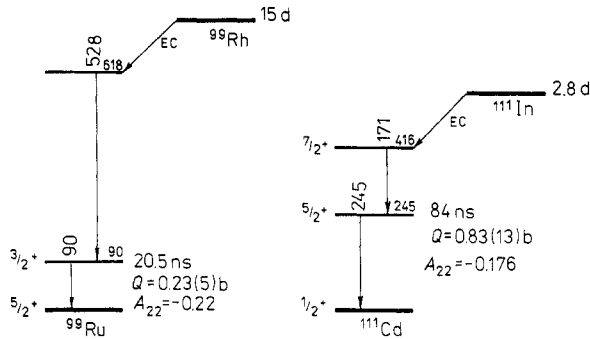


Figure 1. Decay schemes of ^{99}Rh and ^{111}In probes.

So far, considerable interest has been focused on the alloys based on the noble metal hosts. Typical examples are as follows: an attractive interaction between Pd and impurities of s–p elements in the silver host [4] and a repulsive interaction between In–Zn and In–Ga impurity pairs also in the same host [5]. These experimental findings could be at least qualitatively explained in the framework of the conduction electron redistribution caused by the impurity charge excess with respect to the host atoms [6]. Unfortunately this model does not explain differences in the interaction observed for the same impurity pairs in different hosts and of course no such free-electron approach can be applied to dilute alloys based on the transition elements. Recently a more universal model has been applied for a large variety of alloys including the iron-rich alloys [1]. In this approach the impurity interaction is related to the heat of formation of the corresponding alloys which can be calculated using the semi-empirical model in [7].

The experimentally proved attractive interaction between impurities of Rh and some s–p elements in Ag, Cu and Fe matrices agrees with the negative binding energy derived for these systems from the expression in [2]. On the other hand, the model predicts the repulsive interaction for the same impurity pairs in the palladium host. The aim of this work was to establish the nature of the impurity pair interaction for Rh and impurities of 5p series elements in palladium, taking advantage of two excellent ^{111}In and ^{99}Rh PAC probes.

2. Experimental procedure

2.1. Sample preparation

All investigated alloys were produced by arc melting of 99.999% pure palladium with an appropriate amount of impurities in an argon protective atmosphere. After melting, the samples were cold rolled to targets of about 50 mg cm^{-2} thickness. In the next step, radioactive atoms of ^{111}In or ^{99}Rh (the decay schemes are presented in figure 1) were introduced into the binary alloys in two different ways. A commercially available ^{111}In was implanted in $\text{Pd}_{0.98}\text{Rh}_{0.02}$ alloy by scans using the heavy-ion implanter IONAS [8]. The energy of implantation was 400 keV and the total dose about $10^{12} \text{ }^{111}\text{In}^+$ ions. The samples with the ^{99}Rh probe were produced by diffusion of the radioactive ^{99}Rh into the $\text{Pd}_{0.99}\text{X}_{0.01}$ ($\text{X} \equiv \text{Cd, In, Sn and Sb}$) alloys. The ^{99}Rh activity was produced by irradiation

of ^{99}Ru by the 15 MeV deuteron beam of the Göttingen synchrocyclotron as a consequence of the nuclear reaction $^{99}\text{Ru}(d, 2n)^{99}\text{Rh}$. About 12 mg of enriched powdered Ru were wrapped in an aluminium foil and then irradiated for 10 h with an average beam current of $5 \mu\text{A}$. The chemical separation of the carrier-free ^{99}Rh was performed according to the recipe given in [9]. This process is described in detail also in [10]. A drop of a dilute HCl containing carrier-free ^{99}Rh was put on each alloy and then the samples were heated under a hydrogen atmosphere at a temperature of about 1000 K for 1 h. After this treatment, the samples were very slowly cooled to room temperature. Prior to the PAC measurements, all samples were enclosed in quartz tubes filled with argon.

2.2. PAC measurements

The PAC measurements were performed at several temperatures varying between 570 and 970 K. The temperature range was chosen so as to encompass both the low-mobility region of the host atoms at the lowest temperatures and the approach to a totally random distribution of the impurities at the highest temperatures. The precision and stability of temperatures were within 1 K.

A conventional fast-slow apparatus was used. Each of four NaI(Tl) detectors registered both the start and the stop events. From 12 coincidence spectra $W(\theta, t)$ the usual ratio was determined:

$$R(t) = 2 \frac{W(180, t) - W(90, t)}{W(180, t) + 2W(90, t)} \quad (1)$$

where θ denotes the angle between two detectors and t the time which elapses between the emission of two γ -quanta from the same cascade. The experimental $R(t)$ function is directly related to the time-dependent perturbation factor $G_2(t)$ via

$$R(t) = A_{22}^{\text{eff}} G_2(t). \quad (2)$$

A_{22}^{eff} is the correlation anisotropy A_{22} corrected for the detector size [11]. The perturbation factor $G_2(t)$ contains all the information on the hyperfine interaction between the quadrupole moment and the electric field gradient (EFG) at various lattice sites occupied by the probe nuclei.

In general, the distribution of the EFG in dilute alloys reflects, firstly, the occupation of the lattice shells around the probe by impurity atoms and, secondly, the contribution to the EFG produced by impurities in different shells. In practice, however, the contributions to the EFG due to impurities in distant shells are too small to be observed separately and the contribution of the highest magnitude is only pronounced in the EFG's distribution. The experimental spectra $R(t)$ were then fitted with the following probe-dependent expressions for the perturbation factor: for ^{111}Cd ,

$$G_2(t) = f \sum_{n=0}^3 S_n \cos(n\omega_0 t) \exp(-n\delta t) + (1-f) \sum_{n=0}^3 S_n \exp(-n\delta t) \quad (3)$$

and, for ^{99}Ru ,

$$G_2(t) = f[S_0 + S_1 \cos(\omega_0 t)] + (1-f) \quad (4)$$

where f denotes the fraction of probe nuclei experiencing a well defined quadrupole interaction characterised by the frequency ω_0 . The remaining $1-f$ is the fraction of probe atoms on nearly unperturbed lattice sites. δ accounts for a small broadening of the quadrupole interaction frequency caused by randomly distributed impurities at the

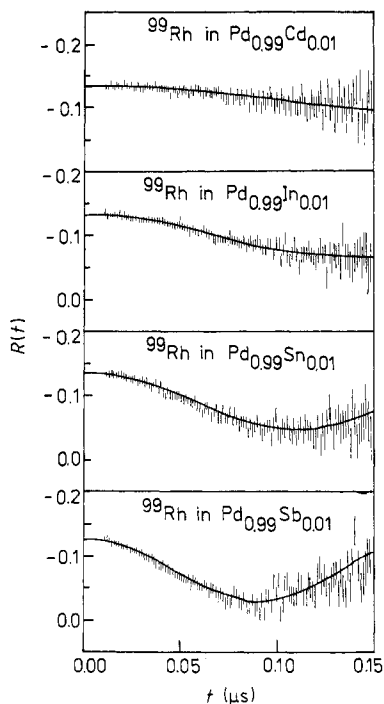


Figure 2. PAC spectra $R(t)$ taken at about 570 K for ^{99}Rh in dilute palladium-based alloys: least-squares fits of equation (4) to the spectra.

sites distant from the probe. The coefficients S_n of the harmonics can be calculated by the diagonalisation of the Hamiltonian of a hyperfine interaction of the EFG with the nuclear quadrupole moment [12]. The difference in $G_2(t)$ for the two probes comes from the different spins I of ^{111}Cd and ^{99}Ru in the intermediate state as well as from the fact that a small broadening δ of the quadrupole interaction frequency was taken into account in the case of the ^{111}Cd probe only.

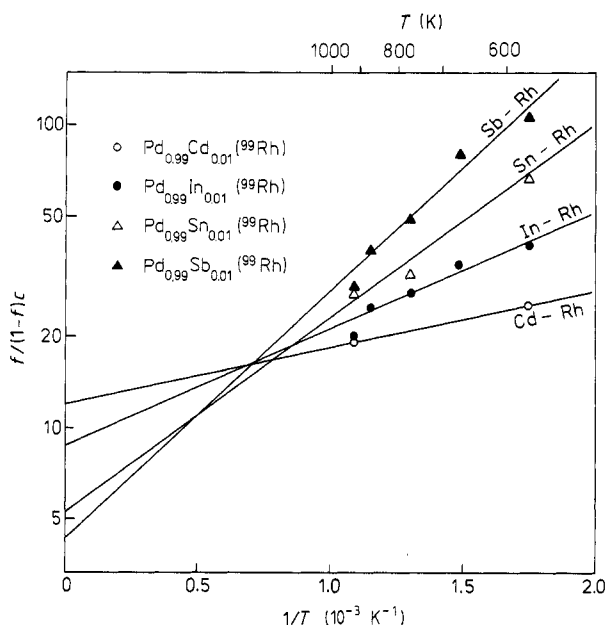
3. Results

The $R(t)$ spectra taken at $T = 570$ K are shown in figure 2 for ^{99}Rh in four Pd-based alloys with Cd, In, Sn and Sb impurities. All the spectra could be fitted with equation (4), i.e. assuming two environments of ^{99}Rh in the alloys. A considerable fraction of the ^{99}Rh probe is exposed to a unique EFG originating in a unique probe–impurity configuration considered here as the nearest-neighbour ^{99}Rh –impurity pair. For the remaining $1 - f$ probes the angular correlation is unperturbed. This indicates that the probes are surrounded by the host atoms only. The fitted values of f and ω_0 are listed in table 1. Since the EFG at lattice sites neighbouring an impurity is known to be insignificantly temperature dependent [13], the spectra taken at temperatures higher than 570 K were fitted with fixed ω_0 and with f as the only free parameter.

For each alloy the fraction f decreases with increasing temperature. Such a temperature dependence is understandable, since the probe–impurity pairs break up at high

Table 1. The fitted parameters f and ω_0 derived from the ^{99}Rh spectra taken at 570 K.

Probe	Alloy	f	ω_0 (MHz)
^{99}Rh	$\text{Pd}_{0.99}\text{Cd}_{0.01}$	0.20(4)	16.7(2.8)
^{99}Rh	$\text{Pd}_{0.99}\text{In}_{0.01}$	0.29(3)	23.6(1.7)
^{99}Rh	$\text{Pd}_{0.99}\text{Sn}_{0.01}$	0.41(1)	28.1(0.9)
^{99}Rh	$\text{Pd}_{0.99}\text{Sb}_{0.01}$	0.51(1)	35.2(1.1)
^{111}In	$\text{Pd}_{0.98}\text{Rh}_{0.02}$	0.45(3)	6.1(0.9)

**Figure 3.** Logarithmic plots of normalised fraction of ^{99}Rh probe forming Rh-impurity nearest-neighbour pair of impurity atoms in dilute alloys of palladium: —, least-squares fits of equation (5) with $\beta = z \exp(\Delta S/k)$ and E_b as two free parameters.

temperatures and the impurity distribution tends to become random. The variation in f with temperature is given by

$$f/(1-f)c = z \exp(\Delta S/k) \exp(-\Delta E_b/kT) \quad (5)$$

where c is the impurity concentration, z is the coordination number ($z = 12$ for an FCC lattice), ΔS is the change in the non-configurational entropy due to the formation of an impurity pair, and E_b is their binding energy [14]. Figure 3 shows the Arrhenius plots of the ratio $f/(1-f)c$ for the systems investigated with ^{99}Rh .

The formation of Rh-In pairs could be observed using two different probes: ^{99}Rh in $\text{Pd}_{0.99}\text{In}_{0.01}$ and ^{111}In in $\text{Pd}_{0.98}\text{Rh}_{0.02}$. According to equation (5) the relative concentration $f/(1-f)c$ of Rh-In pairs should follow the same temperature dependence regardless of the concentration c and of which atom, from two constituents of the pair, is the probe

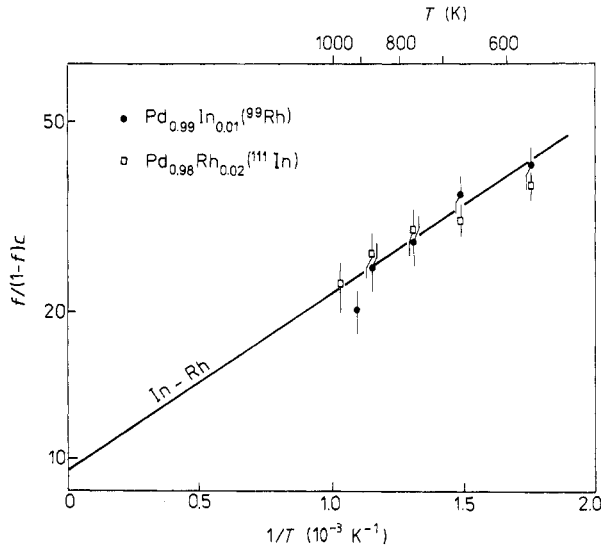


Figure 4. Logarithmic plot of normalised concentration of In-Rh probe-impurity pairs in a Pd host versus $1/T$: ●, $\text{Pd}_{0.99}\text{In}_{0.01}$ (^{99}Rh probe); □, $\text{Pd}_{0.98}\text{Rh}_{0.02}$ (^{111}In probe); —, least-squares fit of equation (5).

Table 2. The entropy β ($=z \exp(\Delta S/k)$) of formation and the binding energy E_b derived from the least-squares fits of equation (5) to the data for relative concentration of impurity-impurity pairs in palladium host. The two last columns represent the binding energy E_b^{bond} calculated using the parameters in [15] and the vibrational contribution ΔS to the entropy of formation for impurity-impurity pair. Data for Ag-In from [16].

Probe-impurity pairs	β	E_b (meV)	E_b^{bond} (meV)	$\Delta S(k)$
Rh-Cd	12.1(4.0)	-36(15)	+72	0.01(30)
Rh-In	9.4(1.9)	-88(11)	+111	-0.24(17)
Rh-Sn	5.3(2.2)	-126(20)	+108	-0.82(35)
Rh-Sb	4.3(1.9)	-161(20)	+104	-1.03(36)
Ag-In	6.1(2.3)	+135(20)	+174	-0.68(47)

and which is the impurity. This is corroborated by the results shown in figure 4, where experimental points taken with ^{99}Rh and ^{111}In lie along a common straight line. The calculated binding enthalpies E_b and entropy changes ΔS are presented in table 2. They were obtained by weighted least-square fits of equation (5) with E_b and $\beta = z \exp(\Delta S/k)$ being two free parameters. From table 2, it is clearly visible that the impurity-pair interaction is attractive (negative E_b) and increases with increasing nominal valence of the impurity atom. In a similar way, the entropy change ΔS varies significantly from zero for Rh-Cd to about $-1k$ for Rh-Sb.

4. Discussion

4.1 Binding energy

Usually, the interaction of metallic elements is discussed in terms of volume and/or electronic properties. Examples are the stability of inter-metallic compounds, the formation of alloys and the variation in lattice parameters with the alloy composition. Of course, both volume and electronic properties are strongly correlated and there are more practical than physical reasons for preferring one argument in order to explain physical findings.

A well known development of this idea was presented in [7, 15] where a semi-empirical model was proposed in order to calculate the heat of formation of transition-metal alloys. The model involves only electronic properties of the constituting metals and treats the atomic interactions as the contact of macroscopic metallic pieces. The atomic volumes enter solely as a measure for the contact surface, but size misfits which could produce an elastic energy contribution are not explicitly considered. In spite of that, the formula for the heat H_{AB} of solution of a metal B in a metal A

$$H_{AB} = [2V_B^{2/3}/(n_A^{-1/3} + n_B^{-1/3})][-P(\Delta\varphi)^2 + Q(\Delta n^{1/3})^2 - R] \quad (6)$$

describes the experimental data quite well. In equation (6), V_B is the atomic volume of the metal B, φ is the electronegativity, $n^{1/3}$ is the cubic root of the electron density at the boundary of bulk Wigner–Seitz cells, and Δ denotes the difference in a given parameter for elements A and B. The coefficients P , Q and R are empirical constants explained in detail in [15].

Following the reasoning presented in [1] the parameters of the above model could be used in order to estimate the binding energy of impurity pairs BC in a host A. When a pair of impurity atoms become first neighbours to each other, a bond with a host atom A is broken for both impurity atoms and a bond between the impurity atoms B and C is created instead. The binding energy E_b^{bond} due to the bond rearrangement could then be expressed as

$$E_b^{\text{bond}} = \Delta E_{BC} - \Delta E_{AB} - \Delta E_{AC} \quad (7)$$

where ΔE_{BC} , ΔE_{AB} and ΔE_{AC} represent the energy of a single bond between BC, AB and AC atoms, respectively. The contributions ΔE could be referred to the heat of formation of the corresponding alloys, i.e. ΔE_{AB} to the heat of solution of the impurity B in the host metal A, and then calculated on the basis of the model in [7, 15].

It was shown that E_b^{bond} -values calculated in this way are in satisfactory agreement with the experimental binding energy for several impurity pairs in Cu, Ag, Au and Fe matrices [1]. In particular, the model predicts an attractive interaction between Rh and s–p metal impurities in a silver matrix in agreement with the experimental findings [10]. We have calculated the binding energy for investigated impurity pairs in palladium using equations (6) and (7). Table 2 contains both experimental and calculated binding energies. Apparent disagreement between them is displayed. We find that even the sign of the binding energy is not reproduced by calculations mentioned above.

Recently, the problem of interaction of impurity atoms dissolved in iron has been discussed [2]. Qualitative agreement between the experimental binding energy with those calculated using equation (6) for a large set of impurity combinations Sn–X ($X \equiv \text{Co, Ni, Cu, Zn, Ga, Ge}$) was obtained [2]. Some deviations were significantly reduced when an additional contribution to the binding energy was postulated. This

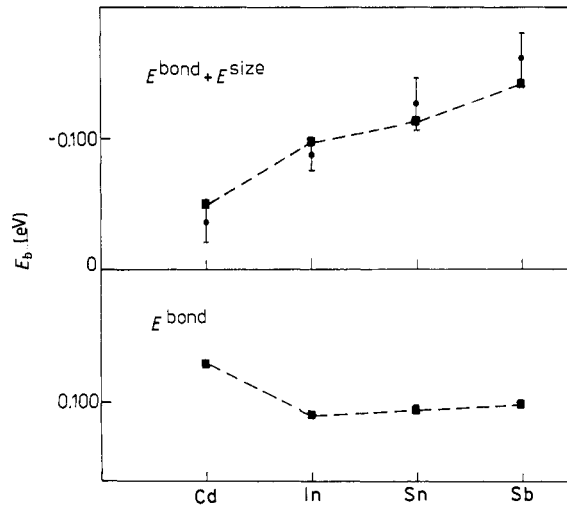


Figure 5. The experimental and calculated binding energy of Rh-X impurity ($X \equiv \text{Cd, In, Sn and Sb}$) in Pd-based alloys.

contribution accounts for the elastic interaction between oversized and undersized impurities in the matrix. The energy due to the size mismatch is proportional to the square of the volume difference [17]. Then the elastic binding energy of a BC impurity pair in a host A can be expressed as [2]

$$E_b^{\text{size}} = \alpha(V_A - V_B)(V_A - V_C) \quad (8)$$

where V_A , V_B and V_C are atomic volumes of the corresponding species and α is a free parameter [2].

A similar contribution to the binding energy could be postulated in the case of the investigated systems. For undersized Rh impurity and oversized Cd, In, Sn and Sb impurities in palladium the elastic interaction contribution is negative. The binding energy written as

$$E_b^{\text{exp}} = E_b^{\text{bond}} + E_b^{\text{size}} \quad (9)$$

could then be reproduced if E_b^{size} is large enough. It is shown in figure 5 that quite good agreement is obtained for $\alpha_{\text{Pd}} = 50 \text{ meV cm}^{-6} \text{ mol}^2$. This number is more than one order of magnitude larger than $\alpha_{\text{Fe}} = 1.7 \text{ meV cm}^{-6} \text{ mol}^2$ derived in [2] for the iron host.

At present we are unable to explain why the α -parameters for Pd and Fe matrices are so different. A possible reason could be overestimation of the elastic contribution due to an incorrect value of the E_b^{bond} . This may happen in particular for the Pd matrix since, according to [7, 15] where the formula given by equation (6) was developed, the data on Pd-based alloys are insufficient to permit a firm statement about the heat of formation for these alloys [15]. The elastic contribution itself does not adequately describe the interaction energy in particular cases, as has recently been noticed for Sn-Be impurity pairs in iron [18]. A doubtful estimation of E_b^{bond} for the palladium host, together with the fact that the expression for E_b^{size} contains a free parameter α , questions the procedure of discussing the binding energy in terms of a simple categorisation of the metals involved.

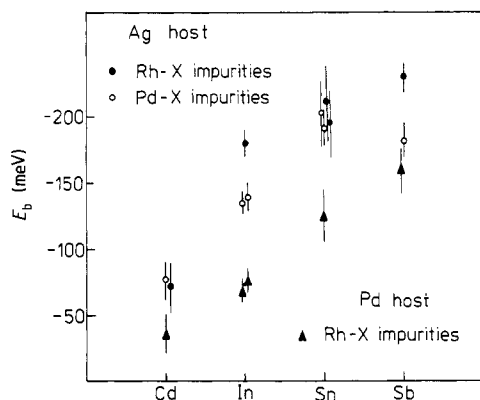


Figure 6. The binding energy for Rh-X and Pd-X ($X \equiv \text{Cd, In, Sn and Sb}$) impurity pairs in Ag and Pd matrices: Double points come from measurements with two different probes for the same impurity pair.

Although the data collected on the binding energy are not very conclusive, one still observes a systematic tendency and a common feature for the impurity interaction in the palladium and the noble metal matrices. An example is shown in figure 6 which contains the experimental data for the binding energy between Rh-X and Pd-X ($X \equiv \text{Cd, In, Sn and Sb}$) impurity pairs in palladium and silver hosts. The binding energy depends on each constituent of the system. The common feature is the attractive interaction for all alloys (all impurity-impurity combinations) and a systematic increase in the binding energy together with the nominal valency of the s-p element.

The experimental findings may be summarised in the following way. Impurity atoms of the last and the one before last element in the d series (Ni, Pd, Pt, Co and Rh) tend to attract impurities of s-p elements in the noble metals, iron and, as was shown above, palladium matrices for all the investigated systems. The repulsive interaction was evidenced in the case of impurity atoms of two s-p elements in the iron [2] and silver [5] hosts as well as between Ag and In impurities in the palladium host [16].

A question of interest concerns understanding the similarity of the interaction character in the five matrices considered. An answer can be drawn from electronic structure considerations relevant to those systems. Unfortunately, such calculations are still lacking. From the experimental data, one may suppose that the effect is related to the electronic structure of the impurity atoms rather than to the host metal. An interaction between 5p valence electrons and 4d electrons of neighbouring atoms leads to energy gain of the system. As an example we consider the attractive interaction between Rh and In and the repulsive interaction between Ag and In in the palladium host. The indium atom with an unfilled p electron shell prefers to be a neighbour to a Rh atom having fewer electrons at the 4d shell than to the palladium host atoms. In the same matrix, an In atom prefers to surround itself with the host palladium atoms with an unfilled 4d electron shell than with an Ag impurity having a completely filled 4d electron shell.

The temperature-dependent PAC measurements yield information about the total pre-exponential entropy term β . As pointed out in § 3, the entropy term β is directly related to the change in the non-configurational entropy during the formation of an impurity-impurity complex.

The data are available mainly for alloys based on the noble metal matrices [1]. Within the limits of experimental error, the entropy of formation of several impurity pairs in

Cu, Ag and Au hosts agrees with the value of 12 (coordination number z for an FCC lattice). This suggests that changes ΔS in non-configurational entropy are negligible. The results obtained in our experiment are considerably different. The values of β as well as $\Delta S/k$ are presented in table 2. $\Delta S/k$ decreases significantly from zero for the Rh–Cd pair to about -1 for the Rh–Sb pair (all in the Pd host). We propose that these non-configurational entropy changes can be due to localised lattice vibration modes. The calculation of the entropy changes due to impurities is a complicated problem ([19] and references therein). This statement is especially valid for impurity pairs. This work presents new valuable results which may have an impact on the work of theoretical physicists.

Acknowledgments

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