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Formation of two-impurity complex in dilute alloys observed through perturbed angular correlations of γ rays

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Interaction between two soluble impurities in metal hosts leads to a nonrandom distribution of the impurity atoms among the lattice sites. The number of the nearest-neighbor impurity-impurity pairs is discussed. It is shown how both the binding energy and the entropy of formation can be extracted for two-impurity complex from the number of these complexes measured as a function of temperature. The method is illustrated by the perturbed-angular-correlation experiment with ^{111}In in dilute alloys of Cu, Ag, and Au with Pt impurity. The entropy of formation found for the In-Pt pair in Cu, Ag, and Au hosts agrees very well with the number of ways in which the pair can be formed in the fcc lattice. The In and Pt impurities are bound, with the binding energy depending significantly on the host.

I. INTRODUCTION

The interaction between impurity atoms in dilute-alloy systems is a problem of primary interest in metal physics. Experimental investigation of this interaction leads to a better understanding of various contributions to the interaction mechanism and to a confirmation of different theoretical approaches. On the other hand it is well known that even a very small concentration of impurities drastically changes the properties of metals and alloys, and therefore the microscopic investigation of the impurity interaction may be of practical importance.

The nature of the impurity interaction is determined by the electronic structure of the dilute alloy. The interaction of the impurity ionic charges screened by the conduction electrons can be attractive or repulsive depending on the relative valence of the alloy constituents and on the distance between interacting impurity atoms. This is a consequence of the oscillatory character of the electron screening potential produced by an impurity net charge upon the conduction electrons.[1]

Among different experimental techniques of approaching the problem of impurity interactions the hyperfine interaction studies give direct information on the local environment of the investigated impurity. A hyperfine-interaction probe introduced in a dilute alloy is exposed to extra nuclear fields of various magnitudes depending on the probe environment in a given system. In a metal with cubic structure an impurity destroys the cubic symmetry and gives rise to an electric field gradient (EFG) which interacts with the nuclear quadrupole moment of the probe atom. The EFG strongly depends on the probe-impurity distance. If the interaction between the probe and impurity atoms favors their specific configuration in the lattice, the EFG corresponding to a given probe-impurity distance can be measured with high accuracy, and a fraction of probes exposed to this EFG can also be determined. In particular, a number of the nearest-neighbor probe-impurity pairs indicates directly the attractive or repulsive character of the impurity interaction.

The use of nuclear radiation as an information carrier makes possible experiments with an extremely low concentration of probe atoms. Main nuclear methods for such investigations are Mössbauer spectroscopy (MS) and the perturbed angular correlations (PAC) of γ rays. For both methods the number of suitable probes is limited. The most important advantage of the PAC method is its constant efficiency in a broad range of temperatures. On the contrary, for many Mössbauer nuclei the measurements are possible only at very low temperatures. The interpretation of the line intensities in the Mössbauer spectra is additionally complicated by the usually unknown Debye-Waller factor for various environments of the probe atoms.

In the past few years perturbed angular correlations of γ rays, particularly those emitted in ^{111}In decay, have been widely applied to study the clustering of lattice defects in metals. The results related to the interaction between ^{111}In and vacancy-type defects in fcc metals have recently been reviewed in Ref. 2. Less attention was paid to the interaction of

^{111}In with impurities in metallic matrices. Still, the attractive interaction was found for In and impurities of some elements in the noble metals[3–5] and the enthalpy (frequently called the binding energy) of formation of the two-impurity complex (In-another impurity) could be determined.

This paper describes the experimental procedure leading not only to the determination of the binding energy but also to the determination of the entropy of formation of impurity pair in metals. General considerations will be illustrated by the PAC experiments performed for copper, silver, and gold matrices with small amounts of platinium and indium impurities.

II. THERMODYNAMICS OF IMPURITY-PAIR FORMATION

We start with a dilute binary alloy $\underline{A}B$ and assume that the element B is soluble in the A matrix over a broad range of concentrations. It means that there is no tendency to form aggregations of atoms B in the A matrix and that thus we can neglect the formation of homogenic BB pairs. We introduce now a trace concentration of probe atoms C to that alloy. If the interaction between C and B inpurities is attractive, their binding energy will be positive and BC pairs will be formed. The formation of CC pairs, even if energetically possible, can be neglected because of the extremely low concentration of probe atoms (10^{-8} or less).

To calculate the ratio of the concentration of impurity pairs to the concentration of their constituents the concept of free energy can be used. The free energy F of a dilute ternary alloy $\underline{A}BC$ due to the presence of isolated impurities B and C and their pairs BC is given by the formula

$$F=E_B(n_B-n_{BC})+E_C(n_C-n_{BC})+E_{BC}n_{BC}-T[S_B^{\text{conf}}+S_C^{\text{conf}}+S_{BC}^{\text{conf}}+S_B(n_B-n_{BC})+S_C(n_C-n_{BC})+S_{BC}n_{BC}]\,, \tag{1}$$

where n_B, n_C, and n_{BC} are the numbers of isolated atoms B, C, and of their pairs BC, E_B, E_C and E_{BC} are the energies per atom or pair, S_B, S_C, and S_{BC} are the nonconfigurational entropies per atom or pair, and S_B^{conf}, S_C^{conf}, and S_{BC}^{conf} are the total configurational entropies of isolated atoms B and C and of their pairs BC, respectively. T is the absolute temperature. The configurational entropies can be calculated as $S^{\text{conf}}=k\ln W$ from the number of ways W_B, W_C, and W_{BC}, in which n_B impurities B, n_C impurities C, and n_{BC} impurity pairs, can be arranged on the N lattice sites of the sample

$$W_B=\frac{N!}{(N-n_B+n_{BC})!(n_B-n_{BC})!}\,,\quad W_C=\frac{N!}{(N-n_C+n_{BC})!(n_C-n_{BC})!}\,,\quad W_{BC}=\frac{(Nz)!}{(Nz-n_{BC})!n_{BC}!}\,, \tag{2}$$

where z is the coordination number of the lattice (for the fcc lattice, $z=12$).

The equilibrium concentration of impurity pairs corresponds to the minimum of the free energy and therefore it can be calculated from the condition

$$\frac{\partial F}{\partial n_{BC}}=0. \tag{3}$$

Minimalization of the free energy given by Eq. (1) and application of Stirling's approximation for the logarithm of the factorial of a large number $N \gg n_B, n_C$ lead to the following formula for the concentration of the impurity pairs:

$$\frac{n_{BC}}{N}=\frac{n_B-n_{BC}}{N}\frac{n_C-n_{BC}}{N}z\exp\left[\frac{S_{BC}-S_B-S_C}{k}\right]\times\exp\left[-\frac{E_{BC}-E_B-E_C}{kT}\right]. \tag{4}$$

$E_{BC}-E_B-E_C=B'$ is the energy which is equal to the difference between the energy of the pair when the impurities are the nearest neighbors and the energy of both impurities when they are surrounded by the host atoms only. $S_{BC}-S_B-S_C=\Delta S$ is the difference in the vibrational entropies for the impurity pair and for the two isolated impurity atoms. Denoting the involved concentrations n_{BC}/N, $(n_B-n_{BC})/N$, and $(n_C-n_{BC})/N$ by c_{BC}, c_B, c_C, and the total entropy term $\beta=z\exp(\Delta S/k)$, the formula (4) takes the form

$$c_{BC}=c_Bc_C\beta\exp(-B'/kT), \tag{5}$$

which has a typical Arrhenius shape. Equation (5) is also derivable from the law of mass action.[6] With the use of this equation one may find the enthalpy and the entropy of formation of impurity pairs from the concentrations of pairs and their constituents. It should be emphasized that the negative sign of B' corresponds to the attractive interaction between impurities. Traditionally, the binding energy B is defined as $B=-B'$ and the negative sign in the exponential function of Eq. (5) vanishes.

III. DETERMINATION OF THE BINDING ENERGY AND THE ENTROPY OF FORMATION FOR IMPURITY PAIRS

Experiments are usually performed on samples with a trace concentration of the γ-ray-emitting probe atoms C dissolved in the dilute binary alloy $\underline{A}B$ with a concentration of element B known from the alloying procedure. This concentration is practically equal to c_B in Eq. (5) because for $n_B \gg n_C$ a number of atoms B bound into pairs BC is negligibly low. The ratio of the remaining two concentrations c_{BC}/c_C is to be determined in an experiment. Two distinct contributions can be observed in the hyperfine-interaction spectra corresponding to the probe atoms isolated in the host matrix and to those bound in probe-impurity pairs. Magnitudes of these contributions are proportional to c_B and c_{BC}, respectively, so the ratio c_{BC}/c_C can be easily found.

Even a single measurement of c_{BC}/c_C performed at a given temperature T makes it possible to determine the binding energy B if the vibrational entropy effects described by ΔS are neglected, i.e., $\Delta S = 0$ and $\beta = z$. Measurements of the temperature dependence yield the information on both the entropy and energy terms. The slope of the Arrhenius plot $\ln(c_{BC}/c_B c_C)$ vs $1/T$ gives the binding energy, and with the use of this value the entropy term can be directly determined. This experimental procedure can be applied under the condition that the equilibrium state is reached at each temperature. It means that the sample must be kept at a given temperature long enough to let the diffusing impurity atoms be trapped into pairs. This imposes a limitation on the lowest temperature at which the measurement can be performed. The annealing time, however, must be reasonable, and in the case of PAC experiments it can not exceed considerably the lifetime of the parent nuclei of the probe.

The high-temperature limit of the measurement range is set by the lifetime of the involved excited state of the probe nucleus. The pairs created cannot live shorter than that lifetime. For typical diffusion coefficients and probes the available temperature range spreads from about 600–1000 K.

There are two ways of performing a measurement of the binding energy B and of the entropy term β: (1) measurement of the concentration ratio c_{BC}/c_C at each annealing temperature, and (2) measurement at low temperature after having frozen the impurity distribution by fast quenching from different annealing temperatures. In the latter case the freezing process should be fast enough to avoid any changes of the impurity distribution during quenching.

The above general considerations will be specified for the case of ^{111}In PAC probes in $\underline{Ag}$Pt alloys. The available temperature range was estimated from known diffusion coefficients. The case of In and Pt impurities in silver is illustrated in Fig. 1. The time of residence of Ag, Pt, and In atoms in a lattice site of silver, τ, was calculated as a function of temperature from the formula

$$\tau = \frac{\lambda^2}{6D}, \tag{6}$$

where λ is a distance of a single jump (in the silver lattice $\lambda = 2.89$ Å) and D is the diffusion coefficient

$$D = D_0 \exp(-Q/kT). \tag{7}$$

The activation energy Q and the coefficient D_0 were taken from literature.[7,8] We neglect the correlation factor in Eq. (6), which for the fast-diffusing In atoms in silver, would make τ slightly shorter than the τ drawn in Fig. 1.

Figure 1 shows that the time of residence for In impurities in silver is longer than the lifetime of the excited state populated in ^{111}In decay (121 ns) below 1050 K and it is shorter than 1 h above 470 K. The temperature range 470–1050 K might be treated as a range of temperatures available for performing the experiment. However, the average time necessary to create an In-Pt pair from randomly distributed impurities is longer than τ because an In atom has to visit several lattice sites during its random walk until it occupies a site in the nearest neighborhood of a Pt atom. Therefore the time of residence of In in a single site should be reduced by a factor $1/zc_B$ which equals 28 for $c_B = 0.003$. Then the low-temperature limit increases and the estimated temperature range spreads from 530 to 1050 K.

Since the diffusion constant value for In impurity in Au is close to that in Ag it is reasonable to assume the same conditions for In-Pt—pair formation in gold. The time of residence of the In impurity in a copper host is considerably longer than in silver and gold, so the available temperature range is 600–1100 K.

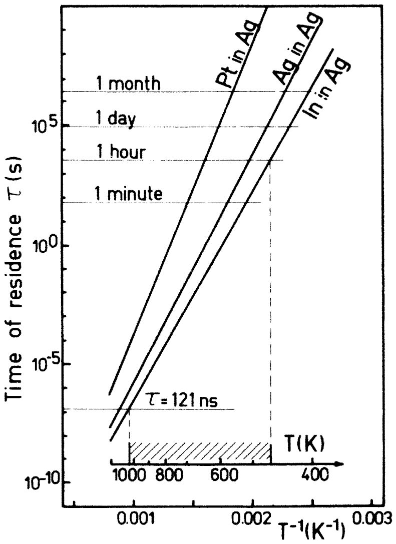

FIG. 1. Average time of residence at a silver lattice site calculated for Pt, Ag, and In atoms from their diffusion coefficients for different temperatures. Indicated interval of temperatures corresponds to the time of residence ranging from 121 ns to 1 h.

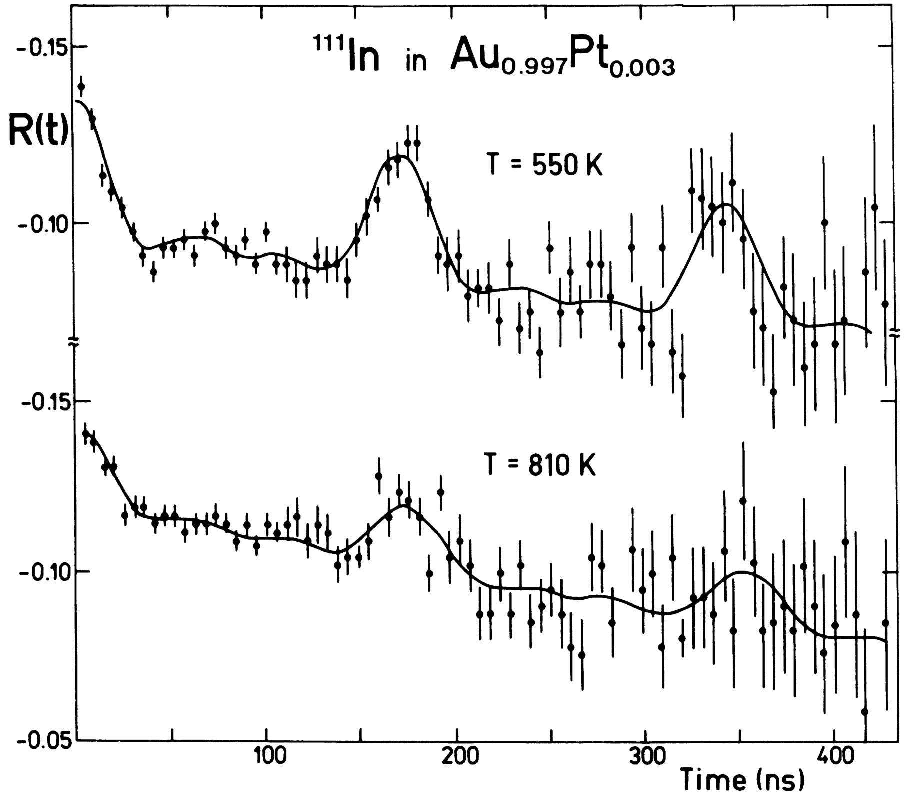

FIG. 2. Perturbed-angular-correlation spectra for ^{111}In in $Au_{0.997}Pt_{0.003}$ taken at 550 and 810 K. Solid lines represent least-squares fits of Eq. (10) to the data.

IV. PAC MEASUREMENTS FOR ^{111}In IN Cu-, Ag-, AND Au-BASED ALLOYS WITH Pt IMPURITY

The ^{111}In activity was produced in natural silver foils by the nuclear reaction $^{109}Ag(\alpha,2n)^{111}In$ with 27-MeV α particles from the Cracow cyclotron. The irradiated foils were placed in the source of the 70-keV isotope separator to implant ^{111}In into Cu or Au. Pieces of these samples were then melted under an argon atmosphere together with appropriate amounts of pure Pt in order to obtain $Au_{0.997}Pt_{0.003}$, $Cu_{0.997}Pt_{0.003}$, and $Cu_{0.99}Pt_{0.01}$ alloys containing traces of ^{111}In of the estimated concentration of about 10^{-9}. A ternary silver-based alloy $Ag_{0.997}Pt_{0.001}In_{0.002}$ was prepared from a piece of the irradiated silver target and appropriate amounts of pure Pt and In metals.

A standard fast-slow coincidence setup with three NaI(Tl) detectors was used to simultaneously record two coincidence time spectra $N(\theta,t)$ for the angle θ between the detectors equal to 180° and 90°. Here, t denotes the time delay between the emission of the 172-keV γ-rays detected by the "start" detector and the emission of the succeeding 245-keV photons detected by the two "stop" detectors. From the measured coincidence counting rates the ratio

$$R(t)=2\frac{N(180°,t)-N(90°,t)}{N(180°,t)+2N(90°,t)} \tag{8}$$

was formed which is directly related to the perturbation factor $G_2(t)$. We have

$$R(t)=A_2G_2(t). \tag{9}$$

$G_2(t)$ contains all relevant information on the hyperfine interactions of the nuclear moments with the extra nuclear fields.[9]

Two derived $R(t)$ spectra for $Au_{0.997}Pt_{0.003}$ are shown in Fig. 2. Obviously the experimental perturbation factor $R(t)$ exhibits a well-defined quadrupole interaction for a significant fraction f of the probe nuclei. The corresponding unique EFG was assigned to the nearest-neighbor ^{111}In-probe—Pt-impurity configuration in the investigated alloys. The remaining probe nuclei have no impurity at the nearest-neighbor sites. The EFG acting on these nuclei is assumed to have a Lorentzian distribution centered around zero due to the impurities located at various different atomic distances. The analysis of all experimental $R(t)$ spectra has then been performed assuming the following expression for the perturbation factor:

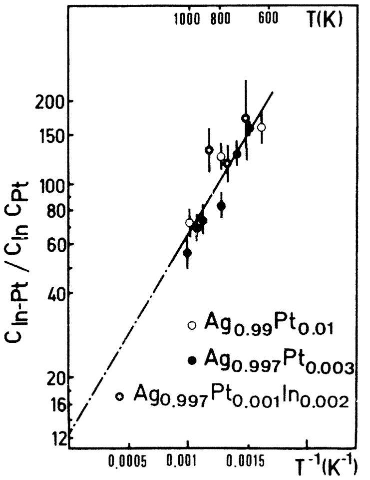

FIG. 3. Logarithmic plot of normalized concentration of In-Pt impurity pairs in an Ag host vs $1/T$. Solid line is least-squares fit of Eq. (5) with β and B as free parameters. Crossing point of the fitted line and the ordinate indicates the value of β.

$$G_2(t)=f\sum_{n=0} S_{2n}\cos(n\omega_0 t) + (1-f)\sum_{n=0} S_{2n}e^{-n\delta t}. \qquad (10)$$

The coefficients S_{2n} are tabulated[9] for the axially symmetric electric field gradient. $\omega_0=(3\pi/10)\times(eQV_{zz}/h)$ contains the quadrupole moment of the probe nuclei eQ and the z component of the EFG V_{zz}. The magnitude of the EFG produced by the Pt impurity in different hosts was discussed in Ref. 10. In order to investigate the formation of the In-Pt pairs the temperature dependence of f, i.e., the fraction of In probes bound to the Pt impurity, was studied for temperatures above 550 K. A decrease in f with temperature appears as a significant decrease in the oscillation amplitude in $R(t)$ spectra for ^{111}In and $Au_{0.997}Pt_{0.003}$ taken at 550 and 810 K shown in Fig. 2. For these two spectra, f equals 0.27(2) and 0.14(2), respectively. The observed ratio $f/(1-f)$ is equal to c_{BC}/c_C, i.e., to the ratio of the concentration of the In probe bound with one Pt impurity to the concentration of In atoms surrounded by the host atoms only. Knowing the nominal Pt concentration c_B the ratio c_{BC}/c_Bc_C was determined. Figures 3 and 4 show values of c_{BC}/c_Bc_C plotted on a logarithmic scale against $1/T$. Data points for $Ag_{0.997}Pt_{0.001}In_{0.002}$ alloys are presented together with the data obtained for ^{111}In in binary AgPt alloys.[4] The expression c_{BC}/c_Bc_C should not depend on the impurity concentration. Indeed, the data points for Ag-based alloys lie on a common straight line independent of In and Pt concentrations.

The straight lines in Figs. 3 and 4 are least-squares fits of Eq. (5) to the experimental data with β and B being free parameters. The values obtained are summarized in Table I.

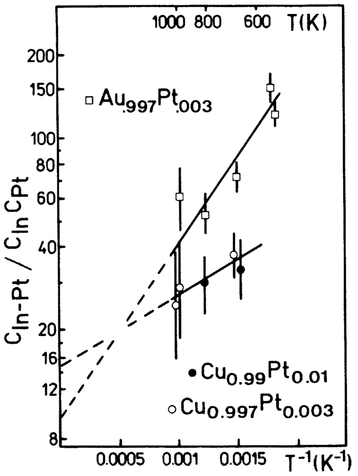

FIG. 4. Logarithmic plots of normalized concentration of In-Pt impurity pairs of Au and Cu hosts vs $1/T$. Solid lines are least-squares fits of Eq. (5) with β and B as free parameters.

V. DISCUSSION

The reported PAC investigation of dilute alloys has demonstrated how to simultaneously extract information on the entropy and the enthalpy of formation of impurity pairs in metals. The values of β listed in Table I are to our knowledge the first reported results on the entropy of formation of a two-impurity complex in metals. Within the limits of experimental error the entropy of formation of In-Pt pairs in all hosts agrees very well with the value of 12 which is expected for configurational entropy only. One may conclude that the vibrational-

TABLE I. Binding energy B and total entropy term β for In-Pt impurity pair in Cu, Ag, and Au hosts.

Host	Systems	Temperature range (K)	B (eV)	β
Copper	$Cu_{0.997}Pt_{0.003}$ $Cu_{0.99}Pt_{0.01}$	660–1015	0.050(18)	14.7(4.4)
Silver	$Ag_{0.997}Pt_{0.003}$[a] $Ag_{0.99}Pt_{0.01}$[a] $Ag_{0.997}Pt_{0.001}In_{0.002}$	620–1010	0.171(9)	12.8(1.0)
Gold	$Au_{0.997}Pt_{0.003}$	550–985	0.124(29)	9.4(5.5)

[a] Data from Ref. 4.

entropy configuration to β is rather small.

More precise determination of β, which would be desirable to prove whether the vibrational-entropy contribution is really negligible, requires very accurate measurements of the fraction of probes forming the impurity pairs in a wide temperature range. As discussed in Sec. III, the range of available temperatures cannot, unfortunately, be significantly extended over that used in the present experiment. Instead, the fraction of the probe-impurity pairs can be determined with high-energy accuracy for systems where (i) the EFG due to the nearest-neighbor impurity is distinctly pronounced in the EFG distribution for different surroundings of the probe atoms, and (ii) the magnitude of this EFG is large enough to result in perturbation-factor oscillations with a period comparable with the lifetime of the respective excited state of the probe nucleus. In this context, the system of a silver host with In and Pt impurities is more favorable than those based on copper or gold because a relatively small fraction of ^{111}In is exposed to the nearest-neighbor EFG in $\underline{\text{Cu}}$Pt and a Pt atom neighboring the probe in $\underline{\text{Au}}$Pt causes oscillations in $R(t)$ spectra with a rather long period.

The present experiment, where all values of β were found to be close to 12, confirms the applicability of the simplified way of binding-energy determination. An analysis of experimental data with the assumption that β is just equal to the lattice coordination number[3,11] makes it possible to determine the binding energy more precisely. For example, values of $B=0.062(8)$ and 0.118(10) eV were obtained for In-Pt pairs in Cu and Au hosts, respectively, when the data were fitted with only one free parameter and with β kept equal to 12. Neglecting the vibrational-entropy effects, the binding energy may then be found even when based on a single measurement of a number of the impurity pairs. The available results for various systems are listed in Ref. 12.

The impurity-pair formation in copper, silver, and gold hosts can be understood as a result of the electronic interaction between the charge excesses of two impurity atoms. Blandin and Deplante[1] showed that the attractive interaction occurs when two different impurity atoms carrying the charge excesses of opposite signs are placed in neighboring lattice sites of monovalent metals. From the positions of Pt and In in the Periodic Table their charge excesses with respect to Cu, Ag, and Au hosts can be estimated to be $+2$ for In and -1 for Pt. Therefore the expected attractive interaction between these impurities is in agreement with our observation. According to Blandin and Deplante the magnitude of the binding energy should practically be the same in all host matrices. As can be seen from Table I the experimental binding energy varies with the host and in the case of silver it is 3 times larger than in the case of copper. This indicates that the simple model based on the electronic interaction does not fully describe impurity-pair formation. On the other hand it has recently been shown[12] that the binding energy involved in the formation of a two-impurity complex is unexpectedly correlated with the heats of formation for bulk materials of the corresponding alloys. It is our hope that the present results add to the existing data and that they will stimulate further investigations to understand the mechanism of impurity redistribution in dilute alloys.

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