Interaction between ^{111}In atoms and impurity atoms of *s-p* elements dissolved in silver

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Perturbed angular correlation measurements were performed with ^{111}In in dilute alloys of Ag with Cu, Zn, Ga, and Ge impurities. It was demonstrated that In atoms attract Cu and repel Zn, Ga, and Ge impurities from its nearest neighborhood in the silver matrix. The energy of this interaction was determined and discussed in the framework of two existing models. The entropy of formation found for the In-Cu, In-Zn, and In-Ga pairs agrees very well with the number of ways in which the pair can be formed in the fcc lattice.

I. INTRODUCTION

The outcome of an attempt to alloy different metals is strongly dependent on the choice of the constituents and, more specifically, on the preference of the constituents to become surrounded with similar or dissimilar neighbors. When there is a weak preference, then atoms of different elements are able to share various sites of a common crystalline lattice. A typical example is a dilute solid solution with impurity atoms occupying the lattice sites of the host metal. In general, the distribution of impurities is not completely random, and experimental studies of this distribution provide the qualitative information on the preference for neighbors in the alloys and also on the energy involved in the formation of an individual impurity-impurity pair.

Among various experimental techniques of approaching the problem in dilute ternary alloys, the hyperfine-interaction studies give direct information on the local environment of a chosen impurity. A hyperfine-interaction probe is introduced as a trace impurity C in a dilute alloy AB and it can monitor changes in its nearest neighborhood caused by differing lattice site occupation of the host atoms A and the impurity atoms B. So far, considerable interest has been focused on the systems in which the attractive interaction was observed, i.e., there was a preference for the impurity B to occupy a lattice site next to the probe atom C. In particular, the attraction between probe and impurity atoms was found in several silver-based alloys with a Au, Pd, Pt, or Rh impurity using an ^{111}In probe[1-3] and containing a Cd, In, Sn, or Sb impurity with ^{100}Pd and ^{99}Rh probes.[4,5]

The attractive interaction was understood as a result of a conduction-electron redistribution due to charge excesses carried by both the impurity and the probe atoms.[6] In another approach, the formation of the probe-impurity pairs in alloys was related to a gain in free energy due to partially ordered impurity distribution.[7-9] Both models give the correct sign of the interaction for the investigated systems and, in most cases, a quite good estimate of the binding energy E_B which determines the strength of this interaction. For the silver host, both models predict a repulsive interaction between impurity atoms of two *s-p* elements.

Evidence for such an interaction between two impurity atoms soluble in the silver host was looked for in this work. In the case of the repulsive interaction, the probe atoms C prefer to surround themselves with the host atoms of silver rather than with the impurity atoms of the element B. Thus, one expects a relatively low concentration of the probe-impurity pairs in the alloy, which may make it difficult to detect a signal. However, the number of probe-impurity pairs should increase with temperature, when the impurity distribution tends to be more random. Investigations in high temperatures are then recommended and, therefore, the perturbed angular correlations (PAC) technique is a suitable experimental method, which reveals a constant efficiency in a broad range of temperatures.

The measurements were performed with the ^{111}In PAC probe in dilute alloys of silver with Cu, Zn, Ga, and Ge impurities. It was demonstrated that the nature of the probe-impurity interaction changes strongly with the impurity charge from a weak attraction for the In-Cu impurity pair to a strong repulsion for the In-Ga and In-Ge impurity pairs.

II. EXPERIMENTAL DETAILS

The binary silver-based alloys were prepared by melting a high-purity Ag foil together with appropriate amounts of Cu, Zn, Ga, and Ge under an argon atmosphere at 1300 K for 1 h. Impurity concentration was 1 at. % for AgCu alloy and 2 at. % for alloys with Zn, Ga, and Ge impurities. The alloys were cold rolled to thin foils (of about 30 mg/cm^2) and were irradiated with 27-MeV α particles at the Cracow cyclotron. The radioactive ^{111}In was produced in targets as a result of the ^{109}Ag(α,2n)^{111}In nuclear reaction. The concentration of the ^{111}In probe was derived from the activity of the irradiated sample. The typical value was 10^{-8}. Alloys of lower impurity concentrations (up to 0.3 at. % for Cu and 1 at. % for the other impurities) were produced by remelting the irradiated samples together with a pure silver foil. The samples were sealed in quartz tubes under an argon atmosphere and then mounted in a small oven in a γ-γ angular correlation apparatus. The time-differential perturbed angular correlation measurements

were performed at several temperatures ranging from 550 to 960 K. The usual ratio $R(t)$ was formed from four coincidence spectra taken with a setup consisting of four NaI(Tl) detectors and standard fast-slow apparatus.[10]

III. RESULTS AND DETERMINATION OF THE BINDING ENERGY

The experimental $R(t)$ spectra were fitted with the perturbation factor consisting of two components corresponding to two different probe-impurity configurations:[10]

$$R(t)=A_2\left[f\sum_{n=0}^{3}S_n\cos(c_n\nu_Q t)+(1-f)\sum_{n=0}^{3}S_n\cos(c_n\bar{\nu}t)\exp(-c_n\delta t)\right], \quad (1)$$

where the correlation anisotropy A_2 is known from nuclear-physics parameters. Here f is the fraction of probe atoms subjected to the quadrupole interaction characterized by the interaction frequency ν_Q. This quadrupole interaction was assigned to the nearest-neighbor probe-impurity configuration and the fraction f has become the relative concentration of the In-impurity pairs in the alloys. The remaining $1-f$ fraction of the probes is exposed to the electric field gradient (EFG) distribution close to zero, generally observed for the probes surrounded by impurities at various atomic distances except the nearest-neighbor sites. For those probes a Lorentzian distribution of the quadrupole interaction frequency was assumed with a width δ and an average value $\bar{\nu}$.

The quadrupole interaction parameters exhibit strong dependence on the type of impurity, and it will be discussed elsewhere. The fraction f depends also on the type of impurity, as well as on the temperature and impurity concentration. For spectra taken at about 600 K, the fraction f equals 0.149(8), 0.027(4), and 0.013(5) for alloys containing 1 at. % Cu, Zn, and Ga impurities, respectively.

If the distribution of probe and impurity atoms over the fcc atoms of Ag is assumed to be random, the fraction of probes with just one impurity as a nearest neighbor would be $f\approx 0.12$ for a 1 at. % alloy. The observed fraction f for AgCu alloys is somewhat higher. This suggests that a number of the nearest-neighbor In-Cu pairs exceeds the value expected for the random distribution and a weak attractive interaction is postulated for In and Cu impurities in silver. In contrast, the concentration of In-Zn and In-Ga probe-impurity pairs in the alloys is much lower than that expected for a random distribution leading to a conclusion of the strong repulsive interaction between these atoms in the same matrix. No unique probe-impurity configuration was evidenced from a smooth distribution of the quadrupole interaction frequency observed for the AgGe alloys. A possible reason would be such a strong repulsion between In and Ge impurities in silver that the number of In-Ge nearest-neighbor pairs falls below a detection limit of the PAC methods.

The temperature dependence of the fraction f is given by[11]

$$f/(1-f)c=Z\exp(\Delta S/k)\exp(-E_B/kT), \quad (2)$$

where c is the impurity concentration, Z is the coordination number ($Z=12$ for fcc lattice), ΔS is the change of the nonconfigurational entropy due to formation of an impurity pair, and E_B is their binding energy. Figure 1 shows the Arrhenius plots of the ratio $f/(1-f)c$ for the investigated systems. A small decrease in f with temperature (upper part) reflects a breakup of In-Cu pairs and an increase of disorder in the AgCu alloys. Distribution of impurities in AgZn and AgGa alloys also tends to become random with increasing temperature but it results in a rise of the In-Zn and In-Ga pairs in silver. So the opposite tendencies in the temperature dependence correspond to the attractive interaction between In and Cu impurities and to the repulsive interaction between In-Zn and In-Ga impurity pairs. The data points lie along common straight lines independent of impurity concentration for each system. According to Eq. (2), a slope of this line derived from the least-squares fit procedure gives the binding energy E_B, and the crossing point with the vertical axis gives the entropy term $\beta=Z\exp(\Delta S/k)$. The fitted values are summarized in Table I.

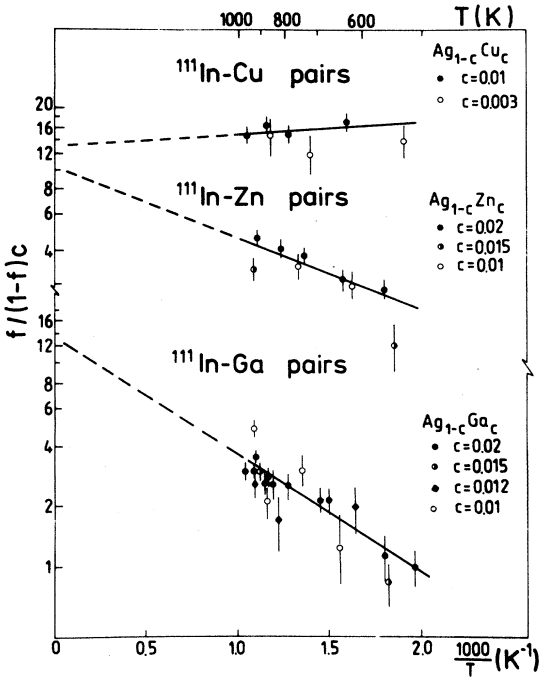

FIG. 1. Logarithmic plots of normalized fraction of the ^{111}In probe forming an In-impurity nearest-neighbor pair of impurity atoms in dilute alloys of silver. Solid lines are least-squares fits of Eq. (2) with β and E_B as free parameters.

TABLE I. The entropy of formation $\beta = Z \exp(\Delta S/k)$ and the binding energy E_B derived from the least-squares fits of Eq. (2) to the data for impurity-impurity pairs in a silver host. The last columns represent the binding energy: E_B^1 is calculated on the basis of the charge-screening model (Ref. 6) and E_B^2 using the method described in Refs. 7 and 9.

Probe-impurity pairs	β	E_B (meV)	E_B^1 (meV)	E_B^2 (meV)
In-Cu	13.5(2.1)	−12(10)	0	4
In-Zn	10.5(2.2)	69(12)	60	38
In-Ga	13.6(2.5)	113(14)	120	44
In-Ge			180	34

IV. DISCUSSION

The investigations reported here have demonstrated the possibility of extracting simultaneous information on the binding energy and on the entropy of formation for a pair of two different impurity atoms which, in particular, tend to repel each other from neighboring lattice sites of the host metal. As was mentioned earlier, the repulsive interaction was suggested by Blandin and Deplante[6] who calculated an electric potential due to an impurity atom introduced into a noble-metal host. It was shown that the impurity-charge-excess with respect to the host, ΔZ, together with the charge of the conduction electrons screening the impurity atom produce the potential $V(r)$, which for large distances ($k_F r \gg 1$) may be expressed as

$$V(r) \sim \Delta Z \cos(2k_F r)/r^3 , \tag{3}$$

where k_F is the Fermi vector. This potential may be attractive or repulsive depending on the sign of ΔZ and the distance from the impurity atom. Within this picture, the binding energy of two impurities is a product of $V(r)$ related to one impurity and the charge excess $\Delta Z'$ of the other impurity placed at a distance r. For the nearest-neighbor distance in the crystal lattice of silver the binding energy equals $0.03 \Delta Z \Delta Z'$ eV.

The charge excesses can be assumed as the valency differences of the impurity and the host atoms to be 0 for Cu, +1 for Zn, and +2 for Ga and In. This leads to $E_B = 0$ for In-Cu pairs and to the positive E_B indicating the repulsive interaction between the In-Zn and In-Ga pairs of impurities in the silver matrix. The calculated binding energy is shown in Fig. 2 together with the experimental values. The presented data reveal full agreement for all three impurity-impurity pairs. In addition, both the model and the experiment suggest a strong repulsive interaction between In and Ge impurities. The quantitative agreement is quite surprising in view of previous attempts to apply this model to the impurity-impurity interaction in other systems. For example, the strong attractive interaction observed in the noble-metal hosts for several impurity pairs consisting of one atom of d element [Pd,[4] Rh,[5] and Pt (Ref. 2)] and one atom of s-p element could be explained qualitatively using the Blandin and Deplante model. However, the calculated binding energy was, as a rule, 2–3 times smaller than the experimental values. Such a quantitative discrepancy may be, to some extent, attributed to the less reliable estimation of the charge state of the transition-metal impurity than the charge excess of Cu, Zn, and Ga impurities in silver taken from the nominal impurity valency.

In another approach to the problem of understanding the impurity distribution in dilute alloys, the binding energy was discussed in terms of the creation and the break-up of the impurity-impurity and impurity-host bonds when the impurity-impurity complex is formed from two impurity atoms surrounded by host atoms only.[7] Accordingly, E_B was written as a sum of three terms:

$$E_B = \Delta E_{BC} - \Delta E_{AB} - \Delta E_{AC} , \tag{4}$$

where ΔE_{BC}, ΔE_{AB}, and ΔE_{AC} represent the energy of a single bond between impurity B and impurity C, host atom A and impurity B, and host atom A and impurity

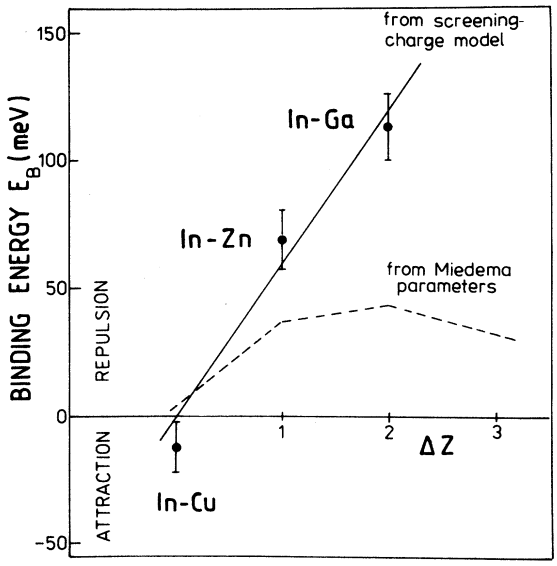

FIG. 2. Dependence of the impurity binding energy on the nominal valence difference ΔZ between the fourth-row elements Cu, Zn, Ga, and Ge and the silver host. The solid line represents predictions of the screening-charge model (Ref. 6) and the dashed line represents E_B calculated using Eq. (4) discussed in the text.

C, respectively. The contributions ΔE_{BC}, ΔE_{AB}, and ΔE_{AC} were referred to the heat of formation for corresponding alloys and then calculated on the basis of the semiempirical model developed by Miedema and coworkers[8] to predict the enthalpy of formation for binary alloys. A difficulty arises when ΔE_{BC} corresponds to an impurity pair consisting of two p elements since, according to the authors, the model does not seem practical in predicting the heat of formation for alloys of two nontransition metals.

Indeed, the agreement between the binding energy given by the experiment and calculated using Eq. (4) is rather poor for In-Zn, In-Ga, and In-Ge pairs of atoms of two polyvalent nontransition metals. A similar effect was observed for Sn-Zn and Sn-Ga pairs of impurities in an iron host by Cranshaw.[9] He postulated an additional contribution to the binding energy due to a size mismatch for the host and impurity atoms. However, such a contribution would have the negative sign for the undersized Zn atom, and the positive sign for the oversized Ga atom both bound to an In impurity in the silver host, and therefore, it could not diminish the discrepancy between the experimental and the model values presented in Fig. 2 (dashed line). The comparison of the measured binding energy and the predictions of two existing models shows much better agreement for the screening-charge model which seems to be particularly suitable for the investigated systems.

Apart from the binding energy, another value derived from the reported PAC measurements is the total preexponential entropy term β. It consists of two components: the configurational entropy Z equal to the number of ways in which the two-impurity complex may be arranged in the lattice, and the vibrational entropy ΔS defined as the difference in the vibrational entropies for the impurity pair and two isolated impurity atoms. For the fcc lattice, the former just equals 12 as the number of the nearest-neighbor sites; the latter, however, is very difficult to calculate. Only scarce information is available in the literature on the entropy changes due to impurities in metals and the complexity of the problem is emphasized.[12] The entropy of formation was determined in a few cases only including In-Pd and In-Pt impurity pairs in silver to be 10.5(1.5) and 12.8(1.0), respectively. These results added to the present data form a set of five values of the entropy of formation for the impurity-impurity pairs in silver with changing character of the interaction from the strong attraction between In and Pt to the strong repulsion between In and Ga atoms. All five values are equal within the limit of the experimental error and are very close to 12, i.e., to the value expected for configurational entropy only. Therefore, one can conclude that the vibrational entropy term ΔS is negligible for a pair of two impurity atoms which interact between each other with attractive or repulsive forces.

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