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Experimental procedure to determine the interdiffusion coefficient of miscibility gap liquid alloys: Case of GaPb system

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An experimental procedure to measure the interdiffusion coefficient of nondilute binary $Ga_{0.6}Pb_{0.4}$ liquid alloys exhibiting a miscibility gap is demonstrated. The phase separation is found to be instantaneous, while the formation of a homogeneous alloy is relatively slow. This technique is based on the measurement of the electrical resistivity of liquid alloys during the formation process in a finite capillary. The concentration profiles, deduced from the electrical resistivity data, combined with the Boltzmann-Matano method [C. Matano, Jpn. J. Phys. **8**, 109 (1933)] were used to determine the concentration dependence of the interdiffusion coefficient.

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I. INTRODUCTION

The diffusion in liquid metals is of great interest for industrial applications such as metal refining and alloying processes. Investigation of diffusion in liquid metals has been the subject of particular attention both from theoretical and experimental points of view (an exhaustive list of references can be found in Ref. 1). The diffusion is usually studied in terms of the diffusion coefficient. Experimental methods for measurements of diffusion coefficient in liquid metals are conventionally classified into two groups:[2] direct and indirect methods. The direct ones use essentially capillary reservoir, shear cell, or electrochemical methods; and the diffusion coefficient is determined using Fick's law.[3] The indirect ones are based on nuclear magnetic resonance or slow neutron inelastic scattering methods, and the diffusion coefficient is calculated from the relaxation parameters that characterize the microscopic transport process.

In this work, we show that an experimental approach can be successfully used to measure the interdiffusion coefficient in nondilute GaPb liquid alloys exhibiting a miscibility gap. This technique employs a finite capillary to measure the electrical resistivity, from which the concentration profile (CP) can be deduced. The interdiffusion coefficient can then be determined from the CP combined with the classical Boltzmann-Matano analysis.[4] It is worth noting that the diffusion equation cannot be solved analytically when the diffusion coefficient varies strongly with composition, as demonstrated in previous work, for instance, the liquid metallic alloys Fe-Ni,[5] Sn-Ag, and Sn-Sb.[6] This is the case for our system, and hence, a numerical approach has been adopted to determine the interdiffusion coefficient of the binary GaPb liquid alloy for different concentrations.

II. METHODOLOGY

The method used in this work is based on the resistivity measurements combined with the Boltzmann-Matano method as described below.

A. Multiprobe cell

The electrical resistivity of GaPb liquid alloys encompassing the critical temperature was measured using a quartz capillary tube of length $h=50$ mm and of internal diameter $\Phi=1$ mm. In order to monitor the gravitational phase separation of the immiscibility gap GaPb system, the capillary was arranged vertically in a horizontal tubular furnace and equipped with evenly spaced electrodes–tungsten wires sealed in the quartz tube (Fig. 1). The furnace has three heating zones and the temperature has been measured with three Alumel-Chromel thermocouples placed at well separate zones on the capillary. With this arrangement, it was possible to maintain the temperature constant (±1 °C) over the full length of the capillary. The geometrical capillary was not perfectly cylindrical; the cell constants of each section of the capillary were initially determined by measuring the resistivity of the triply distilled mercury at room temperature. The relative uncertainty on the resistivity measurement was estimated to be around 1% in the temperature range of 25–800 °C.

Our measurement has been carried out on the Ga_xPb_{1-x} at the critical composition $x_c=0.60$ after the phase diagram of

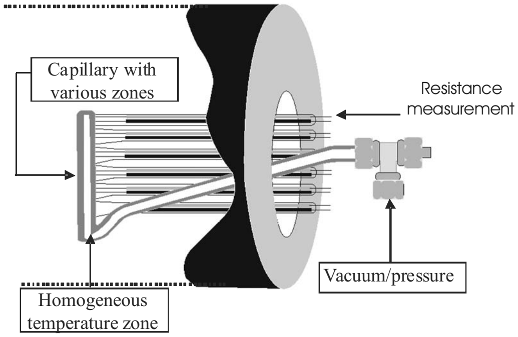

FIG. 1. Schematic picture of the apparatus used for the multiprobe cell resistivity measurement.

Massalski *et al.*[7] The GaPb liquid mixture was protected with argon gas under atmospheric pressure. In order to ensure the homogeneity of our liquid alloy, the liquid was stirred mechanically at 700 °C, much higher than the critical temperature $T_c=606\ ^\circ\mathrm{C}$. This homogeneity has been confirmed by the uniform resistivity value measured across different sections of the capillary.

B. Boltzmann-Matano method

Diffusion coefficients were calculated using the Boltzmann-Matano method,[4] which allows diffusion coefficients to be determined as a function of concentration along the diffusion profile from the equation

$$\tilde{D}(c) = -\frac{1}{2t}\frac{\displaystyle\int_{c_1}^{c} z\,dc}{(dc/dz)_c}, \qquad (1)$$

where t is the time of diffusion, $(dc/dz)c$ is the slope of the concentration-distance profile evaluated at c_1, the integral $\int_{c_1}^{c} z dc$ defines the area between the profile and the Matano interface from $c=0$ to $c=c_1$ concentration lines, and c_1 is any concentration between 0 and 1. This method is presented in more details in Appendix A.

The concentration-distance data at different diffusion times were fitted using a polynomial function. The position of the Matano interface defined by $\int_{c_1}^{c_2} z dc=0$ and the evaluation of the Matano solution [Eq. (1)] at different concentration levels were determined numerically. In fact, the distance between electrodes was not negligibly small (ranging from 3.5 to 8.5 mm), and hence, the uncertainty on the concentration values has been considered and estimated to be between 0.007 and 0.03 depending on the concentration c (see Appendix B).

In the following, the procedure adopted in this work to determine the interdiffusion coefficient of the GaPb liquid alloy is presented and the experimental data obtained are discussed. The calculation of the uncertainty $\Delta D(c)$ on the measurements of the interdiffusion coefficient $D(c)$ is described in Appendix B, and the corresponding values of $\Delta D(c)$ are reported in Fig. 6 as error bars.

III. RESULTS AND DISCUSSION

A. Resistivity versus temperature

Figure 2 shows the temperature dependence of the resistivity of the $\mathrm{Ga_{0.6}Pb_{0.4}}$ liquid alloy corresponding to the critical composition. The measurements were taken while cooling the alloy from 775 to 510 °C. It can be observed that the phase separation occurs at $T_c=610\ ^\circ\mathrm{C}$ and is instantaneous. Above T_c, the resistivity was found to be uniform within the whole length of the capillary, as expected for a homogeneous alloy. Below T_c, the system decomposes into two phases: one rich in gallium (labeled $\mathrm{Ga^{rich}}$-Pb) and the other rich in lead ($\mathrm{Ga\text{-}Pb^{rich}}$) separated by a meniscus defining the interface. The $\mathrm{Ga^{rich}}$-Pb and $\mathrm{Ga\text{-}Pb^{rich}}$ alloys are formed in the upper part and lower part of the capillary, respectively, due to gravitational effect. The resistivity was measured at ten selected sections as shown in Fig. 1. The first five sections are situated in the $\mathrm{Ga^{rich}}$-Pb phase, the sixth section at the meniscus level, and the remaining four sections in the $\mathrm{Ga\text{-}Pb^{rich}}$ phase. The resistivity related to $\mathrm{Ga^{rich}}$-Pb phase sections decreases, whereas those of the $\mathrm{Ga\text{-}Pb^{rich}}$ phase increases. It is interesting to note that the resistivity at the meniscus section shows a typical behavior similar to that observed by Schürmann and Parks[8] in Li-Na and Ga-Hg liquid alloys.

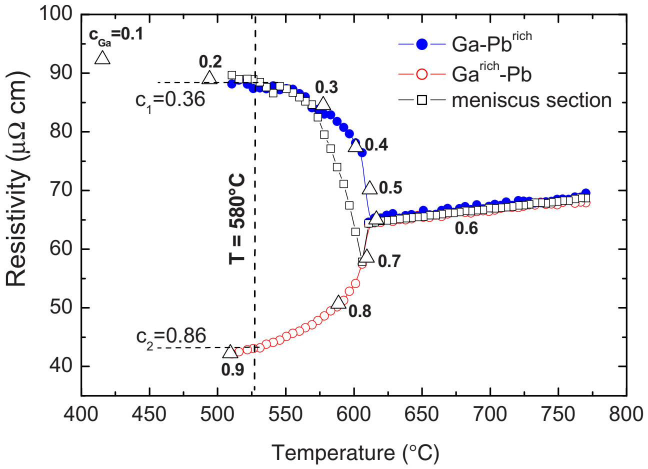

FIG. 2. (Color online) Resistivity versus temperature of GaPb liquid alloys below and above the critical temperature. Triangle symbols are data deduced from the resistivity versus temperature for different concentrations (Ref. 9). The uncertainty on the resistivity is too small (since $\Delta\rho/\rho \approx 1\%$) and so was not included in the figure for clarity.

If we refer to our previous work on the resistivity of the GaPb system for different concentration as a function of temperature,[9] we can relate the resistivity variations below T_c to a change of the concentration at different sections of the capillary. This is illustrated in Fig. 2 by triangle symbols corresponding to a phase separation for each concentration.[9] The gradient of concentration obtained is used to investigate the interdiffusion process of this system. Hence, the temperature of the system was initially fixed at 580 °C, corresponding to Ga concentrations $c_1=0.36$ and $c_2=0.86$ in the lower and upper parts of the capillary, respectively, and then heated rapidly to 720 °C. The resistivity measurements are performed at this latter temperature (720 °C), and the interdiffusion process is observed to be slow as shown in Fig. 3.

The resistivity changes more rapidly with time when approaching progressively the interface region. The resistivity at different zones becomes the same after a relatively long time, estimated to be 4×10^5 s. In fact, the resistivity curves were fitted well by a simple exponential function of time:

$$\rho_i(t) = \rho_0 + \rho_0^i \exp\left(-\frac{t}{\tau_i}\right) \quad (i=1,\ldots,10), \qquad (2)$$

where $\rho_0=67.0\pm 0.7\ \mu\Omega$ cm is the resistivity of the homogeneous $\mathrm{Ga_{0.6}Pb_{0.4}}$ alloy obtained after a relatively long time, and $\rho_0+\rho_0^i$ is the resistivity at section i (with initial concentration $c_0+c_0^i$) at time $t=0$; while τ_i defines a time constant to reach the homogeneous alloying state. The time constant val-

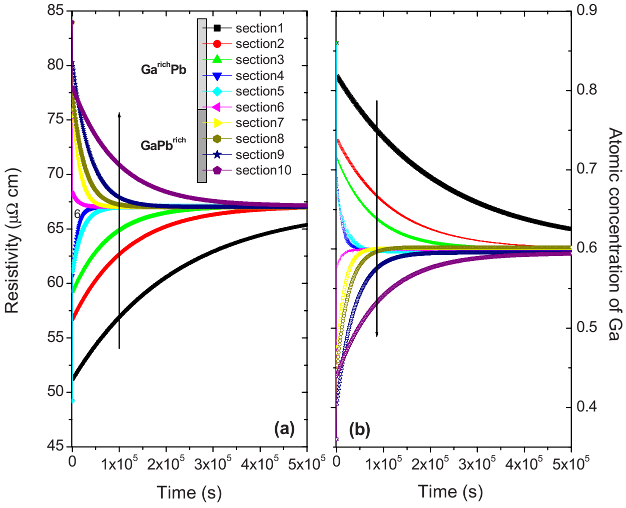

FIG. 3. (Color online) Time dependence of (a) resistivity and (b) concentration of Ga of GaPb liquid alloys at various sections of the capillary. The arrow indicates the resistivity or concentration from section I to section 10. The uncertainty on the concentration Δc is found to be lying between 0.007 and 0.03, corresponding to the initial concentrations $c_2=0.86$ (the highest Ga content alloy) and $c_1=0.36$, respectively.

ues τ_i related to different sections are reported in Table I. It can be deduced from this table that the time constant τ_i increases from the meniscus zone outward. It should be noted that a partial interdiffusion has already taken place during the transient regime when heating the liquid from 580 to 720 °C. The initial concentrations are determined from the present resistivity values at $t=0$ and those reported elsewhere.[9] More precisely, the time dependence of the concentration $c(t)$ at 720 °C was deduced first from resistivity $\rho(c)$ data (Fig. 3 of Ref. 9) by fitting $c(\rho)$ with a third order polynomial:

$$c(\rho) = 1.4905 - 1.0370 \times 10^{-2}\rho - 6.8486 \times 10^{-5}\rho^2 + 3.8224 \times 10^{-7}\rho^3, \quad (3)$$

where c is the atomic Ga concentration. By combining Eqs. (2) and (3), $c(t)$ can be expressed as

TABLE I. Data deduced from the fitting of the time dependence of both concentration and resistivity curves.

Zone	Section i	$\rho_0+\rho_0^i$ ($\mu\Omega$ cm)	$c_0+c_0^i$	τ_i (s)
Ga$^{\text{rich}}$-Pb	1	51.2	0.82	222,736
	2	56.7	0.74	116,484
	3	59.3	0.71	77,656
	4	60.7	0.69	10,645
	5	61.1	0.67	21,022
	6	68.3	0.58	10,659
Interface	7	75.9	0.46	16,059
Ga-Pb$^{\text{rich}}$	8	77.3	0.44	25,595
	9	80.3	0.41	36,928
	10	78.0	0.44	94,410

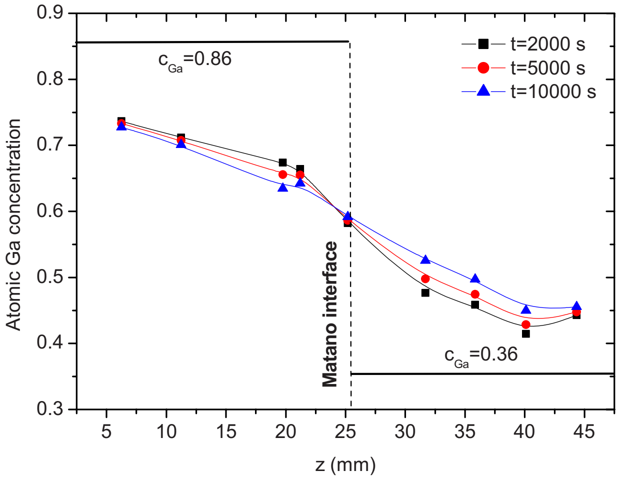

FIG. 4. (Color online) Concentration profile of GaPb liquid alloys.

$$c_i(t) = c_0 + c_0^i \exp\left(-\frac{t}{\tau_i}\right) \quad (i=1,\ldots,10), \quad (4)$$

where $c_0=0.60\pm0.01$ is the concentration of the homogeneous alloy obtained after heating at 720 °C for a relatively long time, and $c_0+c_0^i$ is the initial concentration at section i. The constant τ_i is the same as that defined for resistivity data above (Table I). The interdiffusion coefficient can now be determined from the concentration profiles in the capillary at different times as described by Eq. (4).

Prior to the experiment, the positions of the electrodes have been located very precisely using an optical microscope. The coordinate origin, $z=0$, was fixed at the upper end of the tube, and the position z $(0\leqslant z\leqslant h)$ is taken as the mean distance between consecutive electrodes (h being the length of the capillary). Typical concentration profiles for three different times ($=2\times10^3$, 5×10^3, and 1×10^4 s) are displayed in Fig. 4.

The utilization of the Boltzmann-Matano method assumes that the concentrations can be expressed in terms of the Matano variable $z/\sqrt{t}$, and are independent of time or position.[10] This is valid provided the interdiffusion coefficient $\tilde{D}$ is a function of c only. Furthermore, this analysis also assumes that over the range of compositions considered, the molar volume is constant. It is assumed that the molar volumes remain constant for Ga and Pb, with respective values of 12.72 and 20.50 cm^3/at. g at 720 °C. Therefore, a negligible error on the value of the atomic interdiffusion coefficient deduced from the molar counterpart is expected. The plot of c versus $z/\sqrt{t}$ is displayed in Fig. 5, showing good agreement for a region around the Matano interface within the uncertainty. It is to be noted that the c profile at the interface zone shows an anomalous behavior. This is presumably caused by the interfacial tension with a meniscus profile at the interface as illustrated in Fig. 2.

Our calculation of $\tilde{D}$ shall be considered at zones encompassing the interface region using the profiles of Fig. 4.

From the results reported above on the concentration profile and Boltzmann-Matano method [Eq. (1)], one can evalu-

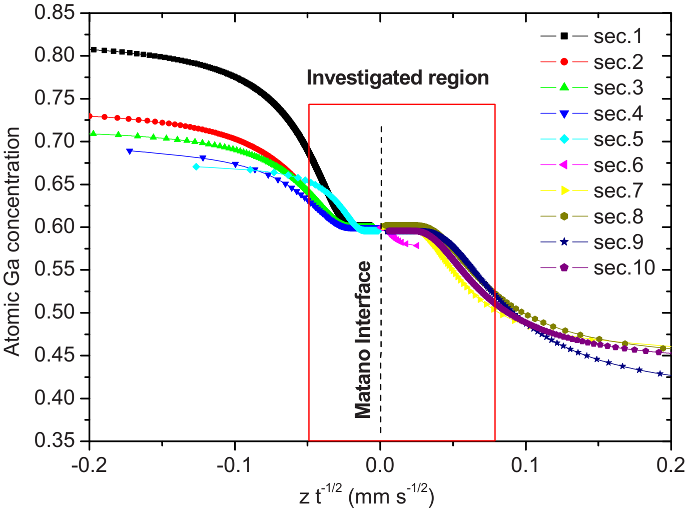

FIG. 5. (Color online) Ga concentration versus time compensated distance of GaPb liquid alloys. The investigated zone is delineated.

ate the interdiffusion coefficient. The Matano interface position is determined to be $z_0 = 0.252$ cm, corresponding to the composition $c_{\mathrm{Ga}}(z_0) \approx 0.60$. The results of the interdiffusion coefficient $\tilde{D}$ as a function of Ga concentration is shown in Fig. 6. It exhibits a minimum of value $\tilde{D}_{\mathrm{min}} \approx 1.3075 \times 10^{-6}$ cm^2 s^{-1} at the concentration $c_{\mathrm{Ga}}^{\mathrm{min}} \approx 0.6$. In fact, a similar behavior has been reported previously for SnAg system,[6] and an opposite trend has been observed for the SnSb liquid alloy, exhibiting a maximum in the concentration dependence of the interdiffusion coefficient. The coefficient of interdiffusion exhibits a minimum for SnAg and GaPb liquid alloys because they are miscibility gap systems. Indeed, the interdiffusion coefficient has been estimated according to the approximation relation of[11]

$$\tilde{D} = c_1 c_2 (c_1 D_2 + c_2 D_1)/S_{cc}(0). \tag{5}$$

The divergence of the structure factor at low angles has been observed for other liquid alloys CuPb (Ref. 12) and BiZn,[13,14] which also present a miscibility gap.

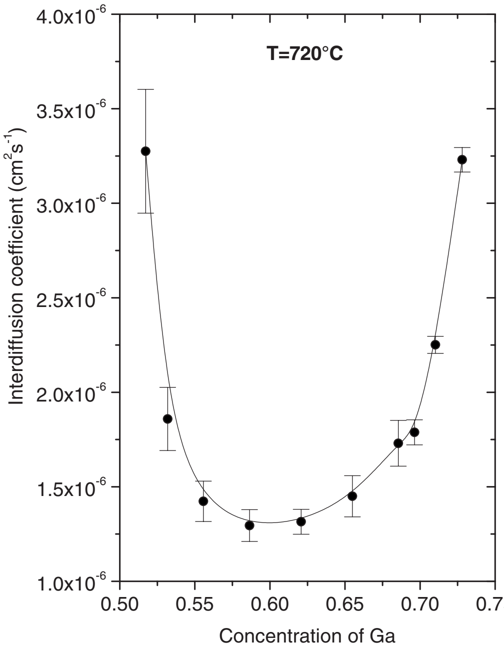

FIG. 6. Ga-concentration dependence of the average interdiffusion coefficient. The solid line is just a guide for the eyes.

In our previous work,[15] we have shown that the segregation of liquid gallium-lead alloy appears clearly by the divergence of the Bhatia-Thornton $S_{CC}(q)$ partial structure factor at q values lower than 0.3 Å^{-1}. Therefore, $\tilde{D}$ is expected to exhibit a minimum at the critical concentration $c \approx 0.60$. One of the drawbacks of the present method is the boundary effects for a relatively short capillary. In order to minimize the boundary effects and for a better accuracy in the resistivity measurements, it would be useful to use a long finite capillary. This would be the perspective of our future work.

IV. CONCLUSIONS

An experimental procedure to evaluate the interdiffusion coefficient in miscibility gap binary systems is demonstrated. This has been successfully applied for the nondilute GaPb liquid alloy. This procedure is based on the measurement of the resistivity of the liquid alloy in a finite capillary and then deducing the concentration profile to evaluate the interdiffusion coefficient by using the Boltzmann-Matano method. The interdiffusion coefficient values of the GaPb liquid alloy versus concentration, in the concentration range of 0.52–0.72, were found to be in the usual range with a minimum $\tilde{D}_{\mathrm{min}} \approx 1.3075 \times 10^{-6}$ cm^2 s^{-1} at critical concentration.

APPENDIX A: BOLTZMANN-MATANO METHOD

The Boltzmann-Matano method is a usual procedure of calculating the diffusion coefficient at each concentration from the diffusion profile. More detailed description of the method can be found in Ref. 4.

The diffusion formula can be expressed as

$$\frac{dc}{dt} = \frac{d}{dz}\left(\tilde{D}\frac{dc}{dz}\right), \tag{A1}$$

where D is the interdiffusion coefficient and c is the concentration.

By using the variable transformation $\lambda = z/t$, Eq. (A1) can be rewritten:

$$-2\lambda\frac{dc}{d\lambda} = \frac{d}{d\lambda}\left(\tilde{D}\frac{dc}{d\lambda}\right). \tag{A2}$$

By integrating Eq. (A2), the following equation is derived, where the slope of the diffusion profile at an arbitrary diffusion depth $z(c)$ is $(dc/dz)_{z=z(c)}$ and the area of diffusion profile under $c(z)$ is $\int_{c_1}^{c} z\,dc$ (Fig. 7):

$$\tilde{D} = \left[-2t\left(\frac{dc}{dz}\right)_{z=z_M}\right]^{-1}\int_{c_1}^{c} z\,dc. \tag{A3}$$

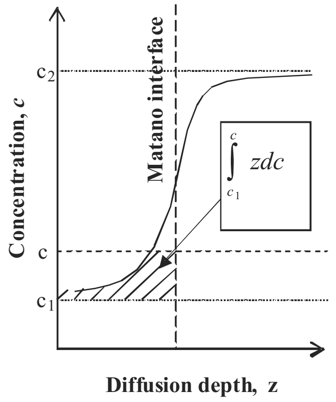

FIG. 7. Schematic figure showing the Matano integral (dashed area).

APPENDIX B: CALCULATION OF THE UNCERTAINTY ON THE INTERDIFFUSION COEFFICIENT

The interdiffusion coefficient $\tilde{D}(c) = -(1/2t) \times [\int_{c_1}^{c} zdc/(dc/dz)_c]$ may be written as $\tilde{D}(c) = -I/2tp$, where the integral I and the slope p are respectively equal to $\int_{c_1}^{c} zdc$ and $(dc/dz)_c$.

The uncertainty on the integral

$$dI(c,c_1) = \frac{\partial I}{\partial c}dc + \frac{\partial I}{\partial c_1}dc_1 + \frac{\partial I}{\partial z}dz$$

with

$$\frac{\partial I}{\partial c} = \frac{I(c+dc) - I(c)}{dc} = \frac{1}{dc}\left[\int_{c_1}^{c+dc} z(c')dc' - \int_{c_1}^{c} z(c')dc'\right]$$
$$= z(c)$$

and $\partial I/\partial c_1 = -z(c_1)$.

Calculation of $(\partial I/\partial z)dz$:

$$\frac{\partial I}{\partial z}dz = I[z(c') + dz(c')] - I[z(c')]$$
$$= \int_{c_1}^{c} [z(c') + dz(c')]dc' - \int_{c_1}^{c} z(c')dc'$$
$$= \int_{c_1}^{c} dz(c')dc'.$$

If we assume that $dz(c')$ is constant on the whole concentration c' range, then

$$\int_{c_1}^{c} dz(c')dc' = dz\int_{c_1}^{c} dc' = (c - c_1)dz.$$

That leads to $(\partial I/\partial z)dz = (c - c_1)dz$.

The uncertainty on the slope $p(c')$:

$$dp(c) = d\left(\frac{dc(z')}{dz'}\right)_{z'=z} = p(z+dz) - p(z)$$

with

$$p(z+dz) = \left(\frac{dc(z')}{dz'}\right)_{z'=z+dz}$$
$$= \left(\frac{dc(z')}{dz'}\right)_{z'=z} + \left[\frac{d}{dz'}\left(\frac{dc(z')}{dz'}\right)\right]_{z'=z} dz.$$

Finally,

$$dp(z) = \left(\frac{d^2c(z')}{dz'^2}\right)_{z'=z} dz.$$

Finally, the uncertainty $\Delta\tilde{D}/\tilde{D}$ on the coefficient $\tilde{D}$ from

$$\Delta I(c,c_1) = \left|\frac{\partial I}{\partial c}\right|\Delta c + \left|\frac{\partial I}{\partial c_1}\right|\Delta c_1 + \left|\frac{\partial I}{\partial z}\right|\Delta z$$
$$= |z(c)|\Delta c + |z(c_1)|\Delta c_1 + |c - c_1|\Delta z$$

and

$$\Delta p(z) = \left|\left(\frac{d^2c(z')}{dz'^2}\right)_{z'=z}\right|\Delta z$$

is as follows:

$$\frac{\Delta\tilde{D}}{\tilde{D}} = \frac{\Delta t}{t} + \frac{\Delta I}{I} + \frac{\Delta p}{p}$$
$$= \frac{|z(c)|\Delta c + |z(c_1)|\Delta c_1 + |c - c_1|\Delta z}{-2tp\tilde{D}} + \frac{\left|\left(\frac{d^2c(z')}{dz'^2}\right)_{z'=z}\right|\Delta z}{p}$$
$$= \frac{|z(c)|\Delta c + |z(c_1)|\Delta c_1}{-2tp\tilde{D}} + \left[\frac{\left|\left(\frac{d^2c(z')}{dz'^2}\right)_{z'=z}\right|}{p} - \frac{|c - c_1|}{2tp\tilde{D}}\right]\Delta z,$$

where $\Delta z \approx 1$ mm and assuming $\Delta t/t \approx 0$.

The uncertainty Δc on the concentration c is deduced from Eq. (3) as

$$\Delta c(\rho) = (1.0370 \times 10^{-2} + 1.36972 \times 10^{-4}\rho + 1.14672 \times 10^{-6}\rho^2)\Delta\rho.$$

Considering the relative uncertainty $\Delta\rho/\rho$ ($\approx 1\%$) on the resistivity ρ, where 40 $\mu\Omega$ cm $< \rho <$ 90 $\mu\Omega$ cm (see Fig. 2), Δc is found to be lying between 0.007 and 0.03, corresponding to the initial concentrations $c_2 = 0.86$ (the highest Ga content alloy) and $c_1 = 0.36$, respectively. Finally, the uncertainty $\Delta\tilde{D}(c)$ is displayed in Fig. 6 as error bars.

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